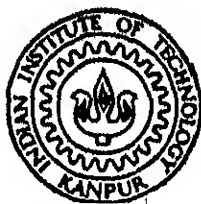# SULFUR MEDIATED INDUCED ELECTRON TRANSFER REACTIONS IN THE CHEMISTRY OF THIOTUNGSTATES

by

MOHD ASIM ANSARI

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

OCTOBER, 1986

SULFUR MEDIATED INDUCED ELECTRON TRANSFER REACTIONS IN THE CHEMISTRY OF THIOTUNGSTATES

A Thesis Submitted

In Partial Fulfilment of the Requirements

for the Degree of

DOCTOR OF PHILOSOPHY

by

MOHD ASIM ANSARI

to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY KANPUR
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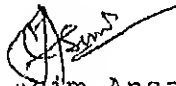## STATEMENT

I hereby declare that the matter embodied in this thesis "Sulfur Mediated Induced Electron Transfer Reactions in the Chemistry of Thiotungstates," is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor S. Sarkar.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Mohd. Asim Ansari

Kanpur.
October 1986.

CERTIFICATE

Certified that the work "Sulfur Mediated Induced Electron Transfer Reactions in the Chemistry of Thiotungstates," presented in this thesis has been carried out by Mr. Mohd. Asim Ansari, under my supervision and the same has not been submitted else-where for a degree.

(S. Sarkar)
Thesis Supervisor
Department of Chemistry,
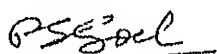IIT-Kanpur

Kanpur
October 1986.

DEPARTMENT OF CHEMISTRY,
INDIAN INSTITUTE OF TECHNOLOGY KANPUR, INDIA

CERTIFICATE OF COURSE WORK

This is to certify that Mr. Mohd. Asim Ansari has satis-
factorily completed all the courses required for the Ph.D.
degree program. The courses include:

Chm 505 Principles of Organic Chemistry

Chm 524 Modern Physical Methods in Chemistry

Chm 525 Principles of Physical Chemistry

Chm 545 Principles of Inorganic Chemistry

Chm 581 Basic Biological Chemistry

Chm 646 Bio-Inorganic Chemistry

Chm 800 General Seminar

Chm 801 Special Seminar

Chm 900 Post-Graduate Research

Mr. Mohd. Asim Ansari was admitted to the candidacy of the Ph.D.
degree in September 1984 after he successfully completed the
written and oral qualifying examinations.

(P. S. Goel)
Head,
Department of Chemistry
Indian Institute of Tech-
nology, Kanpur - 208 016

(S. Sarkar)
Convener,
Departmental Post-
Graduate Committee,
Deptt. of Chemistry,
IIT-KANPUR

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I feel extremely grateful to Mrs. Sarkar for her patience, tolerance and hospitality during my discussions with Professor Sarkar at their apartment.

I offer my sincere thanks to all the faculty members of the department for enlightening me with the various aspects of Chemistry. I wish to make a special mention of Professor S.K. Dogra for his help in allowing me to record electronic spectra in his laboratory. My thanks are due to Prof. S. Chandrasekaran for taking interest in the progress of my work. I am also thankful to him for the helpful discussions and allowing me to use the IR and GC facilities. Timely and generous help given by Prof. A. Chakravorty, IACS, Calcutta, in recording C.V. of some of my samples, is gratefully acknowledged. I feel greatly indebted to Prof. A. Müller, Bielefeld, West Germany for his help in determining X-ray structure and XPS measurements.

It was an experience worth remembering to have worked with Jayanthi, Srini, Udupa and Ramjee. I thank them for their help,

pleasant association and cooperation throughout.

I thank Chaudhury for his pleasant presence in our lab and help in the preparation of the manuscript. I thank all my batchmates and friends especially Hemant, Ranjeet, Manoharan, Pratapan, Islam, Ramaiah, Gupta and Veena for their help and cooperation.

It will be injustice not to recall Dr. S.B.S. Mishra and Dr. M.I. Khan at this moment for their kind advice and encouragement in the initial stage of my work.

I extend my thanks to all the staff members of the department especially to Mr. N. Ahmed for helping me in many ways. I thank Mr. R.D. Singh for the excellent typing of my thesis.

Last but not the least I take the opportunity to acknow-ledge my parents, relatives, teachers, friends and wellwishers for their love, affection, encouragement and patience throughout the course of the work.

Mohd. Asim Ansari

CONTENTS

Contents (contd.)

SYNOPSIS

The thesis entitled, 'Sulfur Mediated Induced Electron
Transfer Reactions in the Chemistry of Thiotungstates,' consists
of four chapters.

Chapter 1 describes a general account of induced intramole-
cular redox processes citing the first example of this type of
reaction from cobalt chemistry and its development to understand
similar reactions involved across M=S bond in the chemistry of
Mo and W.

Conversion of sulfido to persulfido group and vice versa
involving intramolecular electron transfer using external inducing
agents have been correlated with biological systems. A brief
survey of molybdenum-sulfur and tungsten-sulfur compounds has been
presented.

Chapter 2 deals with the scope of the present work. Various
possible modes to invoke induced electron transfer across W=S bond
have been discussed. When chemical stimuli have been proposed to
bring about such reactions, variation of the inducing source and
the suitable changes in the reaction conditions, have been stress-
ed upon. An approach to exploit the utility of induced electron
transfer reactions as synthetic strategy to obtain hitherto
inaccessible compounds of tungsten is outlined.

Chapter 3 describes the experimental procedures and the
details involved in the present work. This chapter has been

divided into five parts. Chapter 3.1 gives an account of the work-up manipulations of the synthesized compounds and the methods used to analyze them. Part 3.2 describes the methods of the preparations of the starting materials used. Part 3.3 presents induced electron transfer reactions brought about by chemical means. Reaction of $W^{VI}OS_3{}^{2-}$ with one or two electron oxidant yields a dinuclear species $[W_2{}^VO_2(\mu\text{-}S)_2(S_2)_2]^{2-}$. However, when $W^{VI}S_4{}^{2-}$ is used as the reactant, the known trinuclear cluster $[W^{IV}S(W^{VI}S_4)_2]^{2-}$ or $[W^{IV}O(W^{VI}S_4)_2]^{2-}$ is formed depending upon the reaction conditions. When $[W_2{}^VO_2(\mu\text{-}S)_2(S_2)_2]^{2-}$ is treated with polysulfide solution it reverts back to $W^{VI}OS_3{}^{2-}$, where poly-sulfide functions as an external reductant. The anion $[W_2{}^VO_2(\mu\text{-}S)_2-(S_2)_2]^{2-}$ reacts readily with activated acetylene to give dithio-lene complex anion, $[W_2{}^VO_2(\mu\text{-}S)_2(S_2C_2R_2)_2]^{2-}$ (R = COOMe, COPh). Reaction of $W^{VI}S_4{}^{2-}$ with activated acetylene gives trisdithiolene complex anion, $[W^{IV}(S_2C_2R_2)_3]^{2-}$. Reaction of $[W_2{}^VO_2(\mu\text{-}S)_2(S_2)_2]^{2-}$ and excess CN$^-$ produces $[W_2{}^VO_2(\mu\text{-}S)_2(CN)_6]^{4-}$ anion. Part 3.4 deals with the synthesis of the compounds which apparently seem to be formed by ligand based redox processes. Reaction of di-alkylaminium salts of oxotrithiotungstate and tetrathiotungstate with excess CS_2 in the presence of air, at room temperature gives heptacoordinated air stable persulfido complexes, $[W^{VI}O(S_2)(S_2CNR_2)_2]$ and $[W^{VI}S(S_2)(S_2CNR_2)_2]$, respectively. However, treatment of $(R_2NH_2)_2W^{VI}S_4$ with controlled amount of CS_2 yields the anionic compound, $(R_2NH_2)[W^{VI}O(S_2)_2(S_2CNR_2)]$. The neutral complexes, $[W^{VI}O(S_2)(S_2CNR_2)_2]$ and $[W^{VI}S(S_2)(S_2CNR_2)_2]$ when reacted with

KCN undergo reductive elimination yielding $[W^{IV}O(S_2CNR_2)_2]$. This coordinatively unsaturated complex reacts with elemental sulfur in an oxidative addition fashion, reverting back to $[W^{VI}O(S_2)-(S_2CNR_2)_2]$. Part 3.5 covers thermally induced electron transfer reactions. Reaction of $(R_2NH_2)_2W^{VI}OS_3$ and $(R_2NH_2)_2W^{VI}S_4$ with CS_2 under reflux condition results in the formation of dinuclear neutral complexes $[W_2^V O_2(\mu-S)_2(S_2CNR_2)_2]$ and $[W_2^V S_2(\mu-S)_2(S_2CNR_2)_2]$ respectively. The same products are obtained when $(NH_4)_2W^{VI}O_2S_2$ and $(NH_4)_2W^{VI}S_4$ are treated with tetraalkylthiuram disulfide at high temperature. Mononuclear complexes, $[W^{VI}O(S_2)(S_2CNR_2)_2]$ and $[W^{VI}O(S_2)_2(S_2CNR_2)]^-$ undergo disproportionation, by thermal means, yielding the dinuclear compound $[W_2^V O_2(\mu-S)_2(S_2CNR_2)_2]$. $[W_2^V OS(\mu-S)_2-(S_2CNR_2)_2]$ reacts with KCN to give $[W_2^V O_2(\mu-S)_2(S_2CNR_2)_2]$.

First part of the Chapter 4 presents the strategies involved in the synthesis of the complexes mentioned above, in terms of intramolecular electron transfer reactions. Synthesis of $[W_2^V O_2(\mu-S)_2(S_2)_2]^{2-}$ from $W^{VI}OS_3^{2-}$ involves the conversion of four sulfido groups to two persulfido groups and sharing of the electrons released by internal oxidant, W(VI) and external oxidant, I_2, $S_2O_8^{2-}$, ROOR or RSSR, equally. In case of WS_4^{2-}, two electron reduction takes place at the same metal center, yielding trinuclear cluster $[W^{IV}S(W^{VI}S_4)_2]^{2-}$ or $[W^{IV}O(W^{VI}S_4)_2]^{2-}$ depending upon the reaction conditions.

In the complimentary reaction, the conversion of $[W_2^V O_2-(\mu-S)_2(S_2)_2]^{2-}$ to 2 $W^{VI}OS_3^{2-}$ using S_x^{2-} as an external reductant leads metal to ligand electron transfer. Conversion of two

persulfido to four sulfido groups requires four electrons which
are supplied by internal reductant W(V) and external reductant
S_x^{2-}. Reactions of $[W_2^V O_2(\mu-S)_2(S_2)_2]^{2-}$ with activated acetylenes
and CN^- yield the products which retain the oxidation state of
tungsten of the starting compound. Reaction of $(R_2NH_2)_2WOS_3$ and
$(R_2NH_2)_2WS_4$ with excess CS_2 in the presence of air gives the
neutral products $[W^{VI}O(S_2)(S_2CNR_2)_2]$ & $[W^{VI}S(S_2)(S_2CNR_2)_2]$ having
metal center in the same oxidation state. Involvement of metal
center in intramolecular electron transfer process is confirmed,
as an ESR active, pentavalent monomeric species is formed during
the course of the reaction. On the basis of above observation,
the following scheme has been proposed:
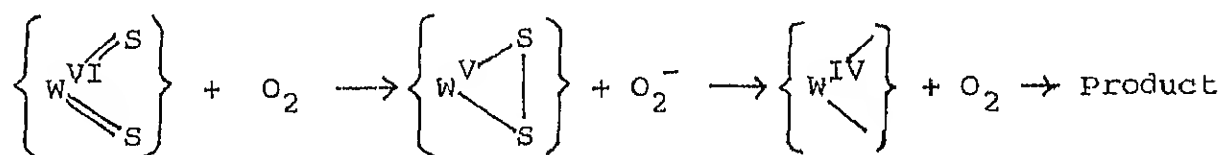
The generation of superoxide radical ion has been verified by speci-
fic chemical reactions.

Formation of $(R_2NH_2)[W^{VI}O(S_2)_2(S_2CNR_2)]$ when limited amount
of CS_2 is used shows that the formation of dithiocarbamate in the syn-
thesis of $[W^{VI}O(S_2)(S_2CNR_2)_2]$ takes place in steps. However, the
same reactants under reflux condition give dinuclear species
$[W_2^V O_2(\mu-S)_2(S_2CNR_2)_2]$, $[W_2^V S_2(\mu-S)_2(S_2CNR_2)_2]$ and $[W_2^V OS(\mu-S)_2-$
$(S_2CNR_2)_2]$ with reduced metal centers. This series of reactions
can best be termed as thermally induced electron transfer reactions.

Thermal induction of $[W^{VI}O(S_2)(S_2CNEt_2)_2]$ results in ligand $\rightarrow$ metal electron transfer and the disproportionation of S_2^{2-} ligand as shown below:
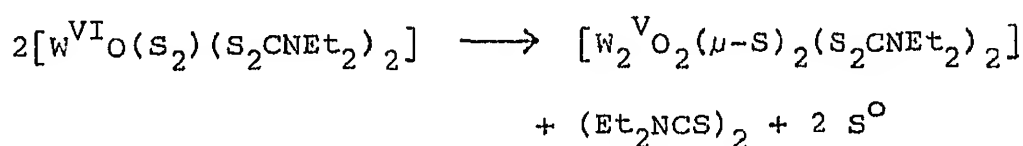
$$2[W^{VI}O(S_2)(S_2CNEt_2)_2] \longrightarrow [W_2^{V}O_2(\mu-S)_2(S_2CNEt_2)_2]$$
$$+ (Et_2NCS)_2 + 2 S^{O}$$

Formation of elemental sulfur could be accounted for through thermal cleavage of S_2^{2-} to S^{2-} and S^{O}.

In the case of $(Et_2NH_2)[W^{VI}O(S_2)_2(S_2CNEt_2)]$, S_2^{2-} ligands do not cleave simply to produce S^{2-} and S^{O} but also induce the reduction of W(VI) to yield W(V) dimer:

$$2(Et_2NH_2)[W^{VI}O(S_2)_2(S_2CNEt_2)] \longrightarrow [W_2^{V}O_2(\mu-S)_2(S_2CNEt_2)_2]$$
$$+ 2 Et_2NH + H_2S + 5 S^{O}$$
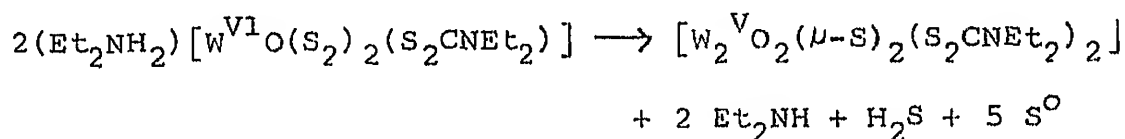
Or precisely the disproportionation reaction is as follows:

$$4 S_2^{2-} \longrightarrow 3 S^{2-} + 5 S^{O} + 2 e^{-}$$
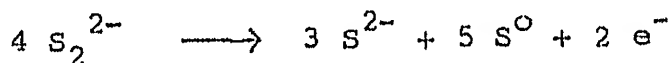
Second part of Chapter 4 describes the physico-chemical and structural investigations of the synthesized compounds described in the preceding chapter. The studies include IR, electronic, ^{1}H NMR, ^{13}C NMR and ESR spectroscopy; C.V. and X-ray crystal structure.

Chapter 1

INTRODUCTION

Electron transfer reactions involving <u>outer-sphere mecha-</u>
<u>nism</u> and <u>inner-sphere mechanism</u> are well documented in the litera-
ture. Pioneering work, in this area has been done by Taube and
co-workers[1-6] In the early sixties of this century, the same
school discovered another class of reactions which involves
intramolecular electron transfer under the influence of some
external agent.[6] This class of reactions was given the name,
"Induced Electron Transfer Reactions." Electron transfer can be
induced by several kind of operations on the ligand. It can be
achieved either by chemical means or by physical stimuli. The
reactions of this type were first studied in cobalt chemistry.
For a better understanding of the nature of this type of react-
ions, the essence of this process is briefly outlined below.

Consider the complex ion

$$[(NH_3)_5CoN\langle O \rangle - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - OH]^{3+}$$
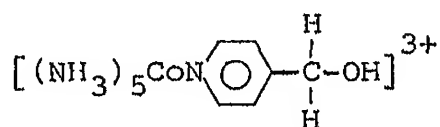
which contains the one-electron oxidizing center Co(III) and a function, the carbinol group, which requires a two electron oxidant for stable product to be formed. Though the metal is in the oxidized state and the carbinol function of the attached ligand is in the reduced state, the intramolecular electron transfer between these two redox active centers is extremely slow because the Co(III) anion complex is a sluggish oxidant to function on a two electron reducing group like carbinol. For the oxidation of the carbinol function, oxidizing agent like Ce(IV), Mn(III) or [Co(III)aq.] having E^O value in the range of 1.5 V is required. The essence of induced electron transfer reaction lies in the fact that the external oxidants having high E^O value are not able to affect the Co(III) center present in the complex directly. They can attack the oxidazable carbinol function with the generation of some reactive species carrying an odd electron, most probably in the form of an organic radical. Thus, under the influence of external oxidant, a reactive intermediate species of the complex can be formed like

$$[(NH_3)_5CoN\langle\bigcirc\rangle - \overset{\overset{H}{|}}{\underset{.}{C}}OH]^{3+}$$
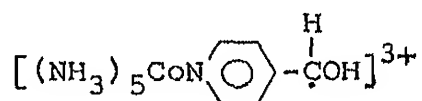
With the presence of this odd electron the internal electron transfer may take place to produce

$$(NH_3)_5Co^{II}N\langle\bigcirc\rangle - \overset{\overset{H}{|}}{C}\diagdown_O + H^+$$
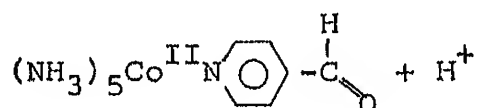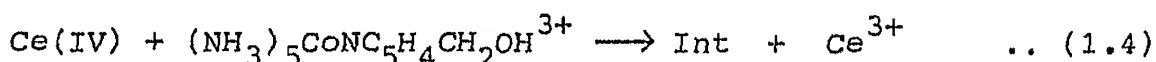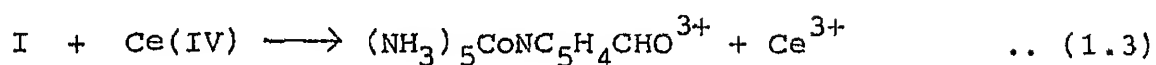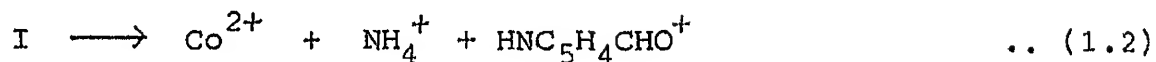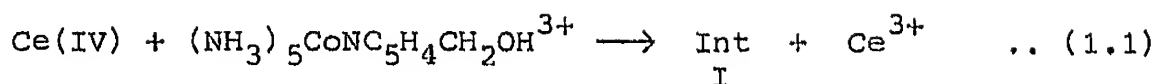
The overall reaction is novel in the sense that under the influence of one electron oxidant as an external source, Co(III) in the complex (internal oxidant) gets reduced at the expense of sharing one electron donated by the carbinol function which changes to aldehyde function. As the generated Co(II) species is very labile to substitution, the complex can dissociate to give Co(II), NH_4^+ and $[HN\langle O \rangle -\overset{H}{\underset{O}{C}}]^+$ in acidic solution. The mode of action of the external oxidant in the present case is to initiate one electron change. The other possibility might exist where the two electron change occurs without formation of a radical or the reduction of internal oxidant (Co(III)).[7]

A direct two electron participation between the external oxidant and the ligand center is then a purely ligand based redox reaction. For induced electron transfer reaction, it is essential to prove that the reduced form of the internal oxidant is among the products of the reaction. Cobalt chemistry is unique in this sense as Co(II) complexes thus formed by induced electron transfer are by large, substitution labile and identification of Co(II) in the reaction medium specially in acidic medium is an easy task. The corresponding Ru(II) system is much less labile than Co(II) and the stability of the reduced intermediate might cause reoxidation by the external oxidant to produce Ru(III) species as the product.[8] Situation of this type might cause difficulties in differentiating the nature of electron transfer reaction between induced electron transfer and purely a ligand based redox reaction.[9]

A very important question regarding induced electron transfer reaction is whether the external and internal oxidants function in concerted manner or the external oxidant acts first to produce reaction intermediate which in turn participates in intramolecular electron transfer. Candlin and Halpern[9] provided the first kinetic data to establish that the internal electron-transfer takes place after the external oxidant has played its role. In some of the reactions using Co(III) complex, when attacked by specific external oxidant say $Cr_2O_7^{2-}$ no radical intermediate is formed and the reaction is a simple ligand based two electron exchange reaction.[10]

The possibility of these two alternative mechanisms i.e., induced electron transfer and ligand based electron transfer reaction taking place in a single reaction has been explored by using a catalyst along with the external oxidant. Thus, Ce(IV) when allowed to function as an external oxidant in the presence of Ag^+ with the 4-pyridinemethanol-cobalt(III) system shows the formation of two intermediates. Kinetic data establish that both the intermediates can undergo internal electron transfer reaction. However, one intermediate undergoes internal electron transfer uninterrupted by the presence of the external oxidant while the other intermediate lives sufficiently long to undergo oxidation by external oxidant in competition with the internal electron transfer reaction. It is clear that two intermediates are formed by parallel events which conclude the following mechanism to

account for the results:[11-14]

$$Ce(IV) + (NH_3)_5CoNC_5H_4CH_2OH^{3+} \longrightarrow \underset{I}{Int} + Ce^{3+} \qquad .. (1.1)$$

$$I \longrightarrow Co^{2+} + NH_4^+ + HNC_5H_4CHO^+ \qquad .. (1.2)$$

$$I + Ce(IV) \longrightarrow (NH_3)_5CoNC_5H_4CHO^{3+} + Ce^{3+} \qquad .. (1.3)$$

$$Ce(IV) + (NH_3)_5CoNC_5H_4CH_2OH^{3+} \longrightarrow \underset{II}{Int} + Ce^{3+} \qquad .. (1.4)$$

$$II \longrightarrow Co^{2+} + NH_4^+ + NHC_5H_4CHO^+ \qquad .. (1.5)$$

$$II + Ce(IV) \longrightarrow (NH_3)_5CoNC_5H_4CHO^{3+} \qquad .. (1.6)$$
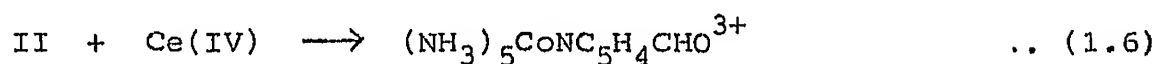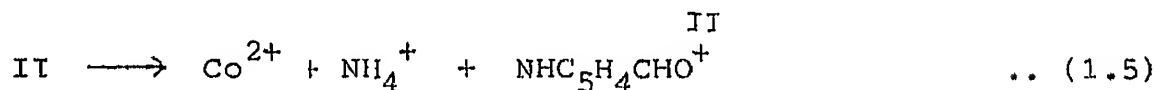
Till early seventies, studies on such reactions were done mainly from the point of view of kinetics. The subject took a new dimension when this methodology was exploited as a strategy to achieve some difficult synthetic goal. In 1975 Deutsch and co-workers reported the synthesis of the first cobalt(III) disulfide complex invoking induced electron transfer process.[15]
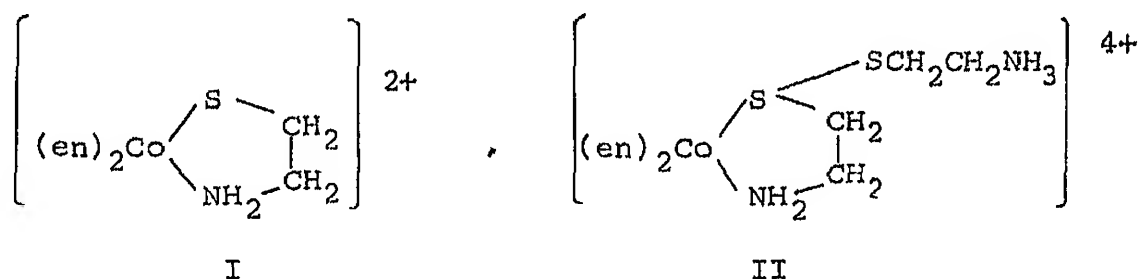
Compound (I) is oxidized by Np^{VI} as:

$$2 (I) + NpO_2^{2+} + 5 H^+ \longrightarrow (II) + Co\ aq.^{2+} + NpO_2^+$$
$$+ 2\ enH_2^{2+} \qquad .. (1.7)$$
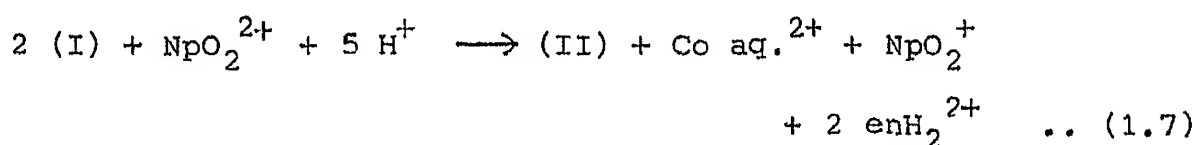
(II) results from (I) by a two electron oxidation, one arising from Np^{VI} and the other arising from a molecule of (I) which in turn is converted to $[Co_{aq.}]^{2+}$. Since most of the metalloenzymes contain sulfur either in the form of sulfide or coordinated thiol, this mode of metal-thiol interaction is relevant to biological systems which contain t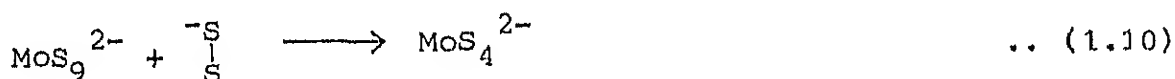he $Fe^{II}-Fe^{III}$ and $Cu^{I}-Cu^{II}$ couples. Subsequently Taube and co-workers[16] exploited this methodology to synthesize disulfide complexes of ruthenium which were not accessible earlier by any other conventional methods.

Thus the exploitation of this chemistry of electron transfer reactions has many facets namely, synthesis of newer complexes which are not accessible by using conventional redox or other reactions and an understanding of the change occurring in the coordinated ligand center along with the participation of the central metal atom. Generally sulfur containing metalloenzymes have sulfur in the form of coordinated thiol groups or as labile inorganic sulfides. Dithiol-disulfide redox centers are present even in many metal free enzymes such as in the stable thioredoxin which forms a hydrogen transferring system with thioredoxin reductase.[17] In xanthine oxidase a persulfido ligand may play a key role in its enzymatic turn over. The ready conversion of molybdenum center from +VI to +IV _via_ +V takes place with the loss of a terminal sulfido group in the oxidation process of the substrates. EXAFS studies[18-20] indicate that the conversion of sulfido group to thiol group results in elongation of the Mo-S bond. Stiefel and co-workers[21,22] correlated the spectroscopic

redox and catalytic properties of the enzyme assuming SR^-
functions as ligand (vide infra):

.. (1.8)
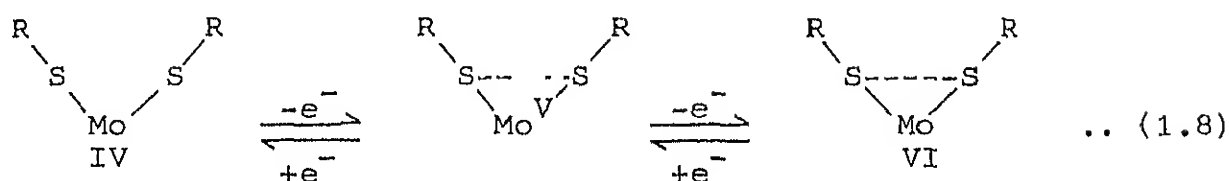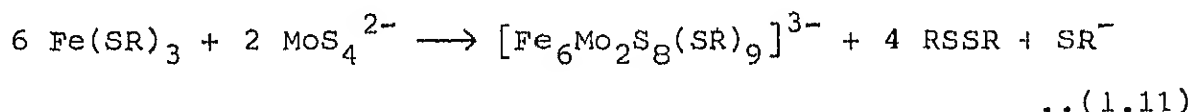
It is inferred that the cis position of molybdenum bound thiolate
can change to a triatomic unit comprising of $\{MoS_2\}$ core with
different degrees of S-S bond formation depending on the redox
state of the molybdenum center. The regeneration stage of the
enzyme under aerobic conditions involves stepwise oxidation with
the intermediate formation of O_2^- which is a complimentary set of
reaction in a reverse manner.[23] Thiomolybdate reactions (1.8)
and (1.10) shown below are complimentary to each other.[24,25]

$$MoS_4^{2-} + S_8 \longrightarrow MoS_9^{2-} \qquad \qquad .. (1.9)$$

$$MoS_9^{2-} + \begin{matrix} ^-S \\ | \\ _-S \end{matrix} \longrightarrow MoS_4^{2-} \qquad \qquad .. (1.10)$$

The high yield reactions of the above type are illustrated exam-
ples of a novel chemistry of molybdeum sulfur systems where a
Mo=S group can be effectively converted into Mo-(S_2) group and
vice-versa. The process involves the change in oxidation state
of molybdenum from VI to IV. Reaction (1.9) is a good example
of induced electron transfer reaction where elemental sulfur
functions as an external oxidant and Mo(VI) in MoS_4^{2-} acts as

an internal oxidant. Here coordinated sulfido group releases
the necessary electrons for the reaction. The complimentary
reaction involves dithiol as an external reductant and Mo(IV)
in MoS_9^{2-} as internal reductant with the reduction of coordi-
nated S_4^{2-} ligands to S^{2-} ligands. In biological processes the
involvement of such redox reactions may be triggered by physical
or chemical stimuli. For induced electron transfer reactions
similar stimulations have already been observed. Metalloenzymes
normally function in conjunction with many electron carrier pro-
teins involving several prosthetic groups. In xanthine oxidase
the molybdenum cofactor operates with flavin and iron sulfur
proteins. Bray and co-workers[26] have shown that the electron
transfer reaction from the substrate to the molybdenum center of
the enzyme is a concerted process. This suggests that the flavin
and iron sulfur prosthetic group of the enzyme function concomi-
tantly with molybdenum cofactor, the binding site of the substrate
of the enzyme. When xanthine dehydrogenase functions the flavin
part is not in operation. Interestingly for its regeneration an
one electron oxidant is necessary. The involvement of flavin in
the regeneration stage of xanthine oxidase by two electron oxi-
dant oxygen,suggests the sharing of the reduction process by
both flavin as well as molybdenum center of the enzyme. Though
in principle, molybdenum in its reduced state i.e. IV can affect
the reduction of oxygen by two electrons, yet the involvement of
flavin to share this redox process is reminiscent of an induction
process where oxygen might play the role of an external oxidant,

which induces the electron transfer _via_ flavin to molybdenum
sulfur bond. The hydroxylation of xanthine to uric acid incor-
porates oxygen from water, and not from the air.[26] It suggests
that the role of oxygen in the regeneration stage of this enzyme
is simply to activate flavin which might induce the electron
transfer across Mo-SR bond with the formation of Mo=S bond in
the oxidized form of the enzyme. Several interesting reactions
in metal sulfur chemistry can be exemplified in terms of induced
electron transfer reactions. Thus the formation of the double
cubane cluster comprised of iron-molybdenum and sulfur is a nice
example in this regard.[27,28]

$$6 \text{ Fe(SR)}_3 + 2 \text{ MoS}_4{}^{2-} \longrightarrow [\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SR})_9]^{3-} + 4 \text{ RSSR} + \text{SR}^-$$

$$..(1.11)$$

In the above reaction iron is as Fe(III) and molybdenum is as
Mo(VI) in the reactants which give the double cubane. It has
been found that four of the iron centers are as Fe(III) and two
as Fe(II) and molybdenum centers are as Mo(III) in the double
cubane. The above reaction may be viewed as induced electron
transfer process as follows:

$$8 \text{ RS}^- \longrightarrow 4 \text{ RSSR} + 8 \text{ e}^- \qquad ..(1.12)$$

$$2 \text{ Mo(VI)} + 6 \text{ e}^- \longrightarrow 2 \text{ Mo(III)} \qquad ..(1.13)$$

$$2 \text{ Fe(III)} + 2 \text{ e}^- \longrightarrow 2 \text{ Fe(II)} \qquad ..(1.14)$$

$$8 \text{ RS}^- + 2 \text{ Mo(VI)} + 2 \text{ Fe(III)} \longrightarrow 4 \text{ RSSR} + 2 \text{ Mo(III)} + 2 \text{ Fe(II)}$$

$$..(1.15)$$
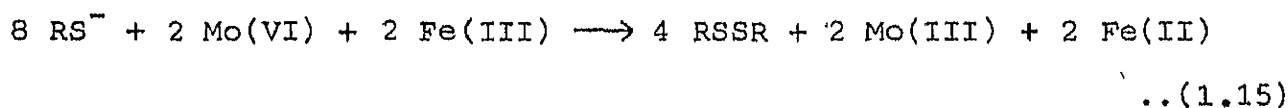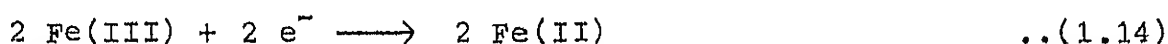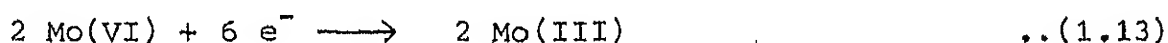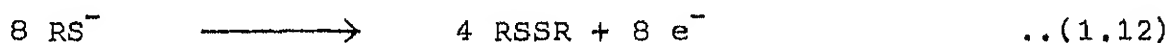
Here MoS_4^{2-} functions as an external oxidant which induces elec-
tron transfer from coordinated SR^- to Fe(III) which represents
the internal oxidant in this process. The electrons donated by
SR^- during its oxidation to RSSR are shared by Mo(VI) and Fe(III)
to form the double cubane. All the reactants after this type of
electron transfer, rearrange to have a thermodynamically stable
heterometallic aggregate. Physical and chemical stimulation of
thiomolybdates and thiotungstates result in the induction of
intramolecular redox reactions across M–S (M = Mo, W) bond. The
use of this type of chemistry as synthetic strategy to isolate
and characterize newer compounds is a recent phenomenon. This
chemistry is not restricted to aqueous medium only. Some interest-
ing results have been obtained using aprotic solvents and even
in the solid state.[31] Table 1.1 gives representative examples of
intramolecular induced redox reactions involved in the isolation
of newer species.

A detailed energy level calculation on $[Mo_2O_2(\mu{-}S)_2(S_2')_2]^{2-}$[29]
implies that the frontier orbitals of the systems are predominantly
Mo and S in character and lie very close in energy. Systems of
this type are most suitable to study thermal or photochemical
activation to induce internal redox reaction. Participation of
a ligand involving these types of excitation processes has been
predicted long back by Taube and co-workers.[10] In fact it has
been observed recently that the conversion of $(NH_4)_2MoS_4$ to MoS_3
upon heating involves metal reduction and ligand oxidation.[30,31]
A photochemical induction using visible light has been recently

reported.[32] This involves the conversion of a Mo(V) sulfido complexes ($Cp_2Mo_2S_4$) to an Mo(IV) disulfido complex [(Cp_2)-$Mo_2S_2(S_2)$]. The involvement of aerial oxygen as an external oxidant to convert $MoS_4{}^{2-}$ to $[Mo_2O_2(\mu\text{-}S)_2(S_2)_2]^{2-}$ at room temperature is an example of the participation of S $\rightarrow$ Mo redox by chemical means[33]. The chemical stimulation of thiomolybdates has been studied using different external oxidants like oxygen, elemental sulfur and organic disulfide. In all these cases the basic reaction is the reduction of molybdenum with the oxidation of the sulfide ligands.[32-35]

The chemistry of heterothiomolybdates is very similar to that of heterothiotungstates with a few exceptions i.e. say when the other heterometal is iron. However, a careful examination of these two systems show similarity in reactivity sometimes. The only difference lies in the more facile reactivity of molybdenum systems compared to that of tungsten systems. Isolation of $[Fe(MoS_4)_2]^{3-}$ [50,51] compared to $[Fe(WS_4)_2]^{2-}$ may be taken as an illustrated example of this behaviour. However, $[Fe(WS_4)_2]^{2-}$ does give $[Fe(WS_4)_2]^{3-}$ under reducing condition and even on long standing in solution wherein the corresponding molybdenum analog is formed more readily even without addition of any external reducing agent.[52,53] No clear explanation for this difference in reactivity may be furnished in some simple norms because the celebrated double cubane clusters comprising of {Fe_6W_2} core is formed in almost identical conditions to its molybdenum analog.[54] A recent report of molybdenum-iron-sulfur cluster

formation of the type $[Mo_2Fe_6S_8(S_2)_2(S-p-C_6H_4Br)_6]^{4-}$ shows that corresponding tungsten analog can not be synthesized under similar conditions, clearly indicating difference in reactivity.[55]

The difference between molybdenum–sulfur and tungsten sulfur systems is wide, when the formation of homometallic cluster compounds are considered. Polythiomolybdates are formed readily using different methodologies. Some representative polythiomolybdates are presented in Table 1.2. The corresponding polythiotungsten compounds are by large yet not known and even if some of them are known, the synthetic strategies are entirely different. Interestingly, the isolation of $W_4S_{12}^{2-}$ and $W_3S_8^{2-}$ has no resemblance in molybdenum systems so far.[44,45] The sluggishness of tungsten sulfur systems may be due to larger separation in energy of the frontier orbitals which are predominantly W and S in character. However, in some cases it can be overcome invoking this newer methodology, induced electron transfer process, as shown in Table 1.1.

Reactions

The reactivity of sulfido and polysulfido compounds of molybdenum and tungsten are varied in nature and the general pattern of these reactions can be described as follows:

Table 1.1 Representative Examples of Induced Electron Transfer Reactions Across M-S bond (M = Mo, W)

Starting Material	Reaction Medium	Inducing Agent	Product	Reference
1	2	3	4	5
$MoO_2S_2^{2-}$	$KOH/H_2S/H_2O$	Thermal, O_2	$[Mo_2^V O_2(\mu-s)_2(s_2)_2]^{2-}$	36
MoS_4^{2-}	s_x^{2-}/H_2O	Thermal	$[Mo_3^{IV} s(s_2)_6]^{2-}$	37
MoS_4^{2-}	s_x^{2-}/H_2O	Thermal	$[Mo_2^V(s_2)_6]^{2-}$	38
MoS_4^{2-}	DMF	Thermal	$[Mo_2^V s_2(\mu-s)_2(s_2)(s_4)]^{2-}$	34
MoS_4^{2-}	DMF	O_2	$[Mo_2^V O_2(\mu-s)_2(s_2)(s_3O_2)]^{2-}$	39
MoS_4^{2-}	CH_3CN	S	$[Mo^{IV} s(s_4)_2]^{2-}$	24
$(NH_4)_2MoS_4$	Solid State	Thermal	$[Mo_2^V(s_2)(s_4)]$	31
$(Cp)_2Mo_2^V s_4$		Photochemical (visible)	$[(Cp)_2Mo_2^{IV} s_2(s_2)]$	32
MoS_4^{2-}	DMF	Thermal	$[Mo^{IV} SMo^{VI}(s_4)_2]^{2-}$	40
MoS_9^{2-}	CH_3CN/DMF	Dithiol	$Mo^{VI} s_4^{2-}$	25
MoS_4^{2-}	DMF	$(PhS)_2$	$[Mo_2^V s_2(\mu-s)_2(s_2)_2]^{2-}$	25
MoS_4^{2-}	H_2O	O_2, $H^+(H_2SO_4)$	$[Mo_2^V OS(\mu-s)_2(s_2)_2]^{2-}$	41
MoS_4^{2-}	CH_3CN	Tetraethyl-thiuram disulfide	$[Mo^V(s_2)(s_2CNEt_2)_3]$	42
WS_4^{2-}	H_2O	H^+	$[W^{IV} O(W^{VI} s_4)_2]^{2-}$	43

...contd.

Table 1.1 (contd.)

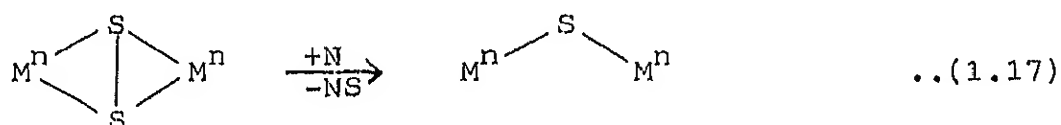| 1	2	3	4	5
WS_4^{2-}	MeOH	H^+	$[W^{IV}S(W^{VI}S_4)_2]^{2-}$, $[W^{II}(W^{VI}S_4)_2]^{2-}$	40 44
WS_4^{2-}	CH_2Cl_2	H^+	$[W_2^{V}S_2(\mu-S)_2(W^{VI}S_4)_4]^{2-}$	45, 46
WS_4^{2-}	DMF	1,2-Ethane dithiol	$[W_2^{V}S_2(\mu-S)_2(edt)_2]^{2-}$	47
WS_4^{2-}	DMF	S	$[W_2^{V}S_2(\mu-S)_2(S_4)_2]^{2-}$	48, 49
WS_4^{2-}	DMF	Thermal,coordinated S^{2-}	$[W^{IV}S(W^{VI}S_4)_2]^{2-}$	40

Table 1.2 Different Types of Polythiomolybdates

Type	Source of sulfur	Starting Material	Product	Reference
$\{Mo_2S_2\}^{2+}$	Starting material	$MoO_2S_2^{2-}$	$[Mo_2^VO_2(\mu-S)_2(S_2)_2]^{2-}$	36
"	"	MoS_4^{2-}	$[Mo_2^VOS(\mu-S)_2(S_2)_2]^{2-}$	42
"	"	MoS_4^{2-}	$[Mo_2^VS_2(\mu-S)_2(S_2)_2]^{2-}$	25
"	Starting material and RSSSR	MoS_4^{2-}	$[Mo_2^VS_2(\mu-S)_2(S_4)_2]^{2-}$	39
"	"	MoS_4^{2-}	$[Mo_2^VS_2(\mu-S)_2(S_2)(S_4)]$	39
"	Starting material	$MoOS_3^{2-}$	$[Mo_2^VO_2(\mu-S)_2(S_2)(S_3O_2)]^{2-}$	40
$\{Mo_3S_4\}^{4+}$	Polysulfide	MoO_4^{2-} or MoS_4^{2-}	$[Mo_3^{IV}S(S_2)_6]^{2-}$	37, 56, 57
"	Starting material	$[Mo_3S(S_2)_6]^{2-}$	$[Mo_3^{IV}S_4(CN)_9]^{5-}$	58
$\{Mo=C_t\}^{2+}$	Elemental sulfur	$MoOS_3^{2-}$	$[Mo^{IV}O(S_4)_2]^{2-}$	34
"	Starting material	$MoOS_3^{2-}$	$[Mo^{IV}C(Mo^{VI}S_4)_2]^{2-}$	43, 59
$\{Mo=S_t\}^{2+}$	Starting material and elemental sulfur or RSSSR	MoS_4^{2-}	$[Mo^{IV}S(S_4)_2]^{2-}$	24
"	Starting material	MoS_4^{2-}	$[Mo^{IV}S(Mo^{VI}S_4)]^{2-}$	41
$\{MoS_2Mo\}^{8+}$	Polysulfide	MoO_4^{2-} or MoS_4^{2-}	$[Mo_2^V(S_2)_6]^{2-}$	38, 60

(i) Oxidation of the ligand by external agents

The synthesis of the complex containing $S_3O_2^{2-}$ ligand $[Mo_2O_2(\mu S)_2(S_2)(S_3O_2)]^{2-}$ from $MoOS_3^{2-}$ and elemental sulfur in the presence of air proceeds according to Scheme (1.16)[61] involving the oxidation of the coordinated S_3^{2-} ligand

$$\{MoO(S^{2-})\} \xrightarrow{S_8} \{Mo(S_4^{2-})\} \xrightarrow{-S} \{Mo(S_3^{2-})\} \xrightarrow{O_2} \{Mo(S_3O_2^{2-})\}$$

$$..(1.16)$$
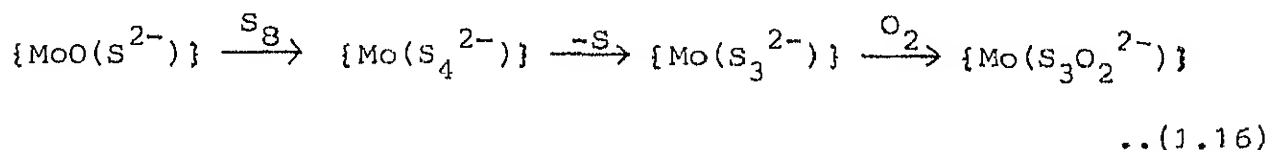
(ii) Reaction with nucleophiles

Abstraction of sulfur atom by nucleophiles (N) such as PPh_3, SO_3^{2-}, SR^-, CN^- and OH^- is the characteristic feature of disulfido and polysulfido complexes. In disulfido complexes abstraction of sulfur atom takes place in the following way:[62-68]

$$..(1.17)$$

Few representative examples are shown below:

$$[Mo_2^V(S_2)_6]^{2-} \xrightarrow{OH^-} [Mo_2^VO_2(\mu\text{-}S)_2(S_2)_2]^{2-} \qquad ..(1.18)$$

$$[Mo_3^{IV}S(S_2)_6]^{2-} \xrightarrow{CN^-} [Mo_3^{IV}S_4(CN)_9]^{5-} \qquad ..(1.19)$$

$$[Mo_2^V(S_2)_6]^{2-} \xrightarrow{SR^-} [Mo_2S_2(\mu\text{-}S)_2(SR)_2]^{2-} \qquad ..(1.20)$$
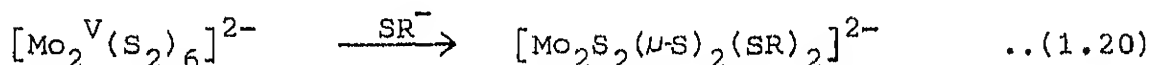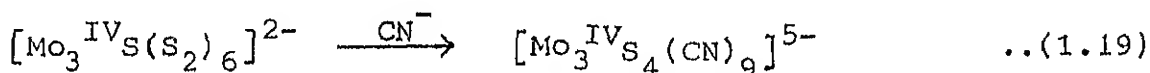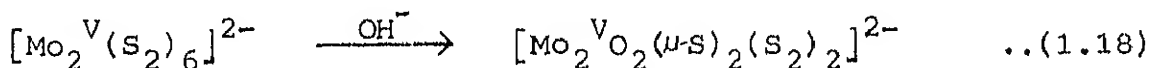
All these reactions involve loss of a neutral sulfur atom from the complex without leading to any change in the formal oxidation state

of the metal atom. These reactions result in the substantial
transfer of electron density from the ligand to the metal so
that the population of the ligand π^* level is decreased.[62-70]
However, reduction of molybdenum center does occur in certain
cases when a strong nucleophile like CN^- is used:[66]

$$\left[Mo_2(V)(S_2)_6\right]^{2-} \xrightarrow{CN^-} \left[Mo_2(III)(\mu\text{-}S)_2(CN)_8\right]^{6-} \quad ..(1.21)$$
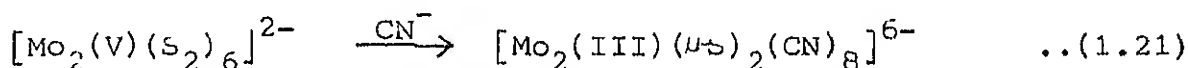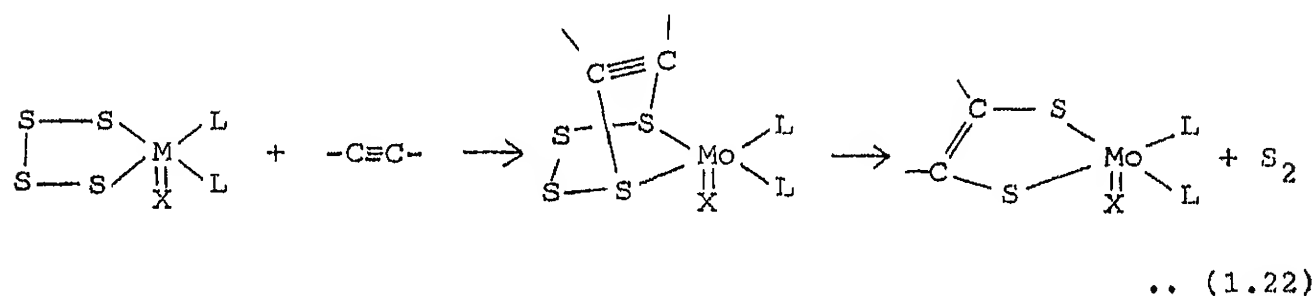
Insertion Reaction

Insertion reactions are of two types i.e. with CS_2 and acti-
vated acetylene. Thus MoS_9^{2-} reacts readily with CS_2 with the for-
mation of $\left[MoS(CS_4)_2\right]^{2-}$ anion. Crystal structure analysis has
shown that this anion exists in cis as well as trans configura-
tion.[71,72] The reaction of $\left[Mo_2S_2(\mu\text{-}S)_2(S_2)(S_4)\right]^{2-}$ with CS_2 leads
to the formation of $\left[Mo_2S_4(CS_4)_2\right]^{2-}$ anion.[71] The easy formation
of CS_4^{2-} ligand from S_4^{2-} is brought about by dissociation of S_4^{2-}
to S_2^{0} followed by interaction with electrophilic molecule CS_2.
The formation of perthiocarbonate ligand with CS_2 is well document-
ed with many other metal polysulfido complexes.[73-75] The reaction
of these complexes with electrophile like 2-butynedimethanoate
(DMA) is highly interesting. Thus when MoS_9^{2-} reacts with DMA,
the trisdithiolene complex $\left[Mo(S_2C_2(COOCH_3)_2)_3\right]^{2-}$ anion is formed.
However, reaction with $MoOS_8^{2-}$ produces the penta-coordinate
complex $\left[MoO(S_2C_2(COOCH_3)_2)_2\right]^{2-}$ anion.[76,77] The formation of
dithiolene type of ligand in the reaction of these complexes with
DMA differs from the reaction of this activated acetylene with

$[Mo_2O_2S_6]^{2-}$ anions.[78] Here insertion of DMA takes place into the Mo-S bond rather than S-S bond with the formation of S-C-coordinated vinyl disulfide ligand. It has been observed that the complex anion $[Mo_2O_2(\mu\text{-}S)_2(S_2)(S_4)]^{2-}$ reacts with DMA at ambient temperature to give the same vinyl disulfide complex. Under refluxing conditions, the reaction affords the dithiolene isomer.[79] It has been proposed that coordinated S_4^{2-} ligand dissociates to S_2^{2-} and S_2^{O} in solution to react rapidly with DMA to form the vinyl disulfide complex which thermally rearranges to the dithiolene isomer. An apparent difference in reactivity between S_2^{2-} and S_4^{2-} ligand has been noticed. X-ray structural data shows that the S-S bond length in this side on bound S_2^{2-} ligand ranges from 2.03 to 2.074 Å and is slightly longer than S-S bond in elemental sulfur S_8. In contrast in the complex containing S_4^{2-} unit, for example, MoS_9^{2-} where S_4^{2-} acts as a bidentate ligand, the S-S bond directly adjacent to Mo atom elongates which can be correlated with the shortening of the corresponding Mo-S bond. This suggests that bonding electron from the S-S bond are transferred to Mo-S bonding orbitals.

The S-S bond length for the uncoordinated S_2^{O}, S_2^{-} and S_2^{2-} are 1.89 Å, 2.00 Å and 2.3 Å, respectively. These data together with the S-S bond length observed in several side on coordinated S_2^{2-} species suggest a bond order 1 for the coordinated S_2^{2-} ligand. This strengthening of bond order would originate by the transfer of electron density from the antibonding π^* orbital to the Mo-S bond. This would result in a net depopulation of the

S_2^{2-} orbitals in these complexes.[80] Furthermore, the π^* nature

of LUMO suggests that a cycloaddition of acetylene to the Mo

side on bound S_2^{2-} would be a symmetry forbidden process. Hence

this cycloaddition reaction of activated acetylene with pure

Mo$\diagdown\!\!\!\begin{smallmatrix}S\\|\\S\end{smallmatrix}$ units are unknown. The only well documented reaction

of DMA with such unit in $[Mo_2O_2(\mu\text{-}S)_2(S_2)_2]^{2-}$ complex ion[78] is

known in which the alkyne has inserted into Mo-S bond. The

formation of dithiolene ligand by the reaction of polysulfido

complexes with activated acetylenes are known.[75] The most likely

mechanism is shown below which involves the cycloaddition of the

electrophilic alkyne to the coordinated S_x^{2-} chelate.

.. (1.22)

Scheme 1.1 Cycloaddition of alkyne to the Mo-S unit

Other Reactions

Reductive elimination reactions are also well known. For

example, $Cs_2[Mo_2^V(S_2)_6]$ thermally responds to generate S_2 mole-

cule as the main gaseous product with the formation of Mo-S

cluster in the lower oxidation state.[69,81] Thermal decomposi-

tion of $(NH_4)_2[Mo_3S(S_2)_6]\cdot nH_2O$ at 270°C produces one mole of

NH_3 and half a mole of H_2S per mole of this trinuclear

compound.[81]

Physical Studies

Sulfido and polysulfido complexes of molybdenum and tungsten have been studied extensively using all the conventional physicochemical methods. Whenever complexity arose, X-ray crystal structures were determined. For a few systems effect of temperature has also been studied.[69,81] There is a trend to study the electrochemical behaviour of such systems. This certainly helps in understanding the mechanistic aspects of metalloenzymes where Mo or W is the active center.[21,26]

Vibrational Spectra

Vibrational spectroscopy has been found to be a very important tool in determining the presence of a particular functional group in such complexes. In most of these cases, it is possible to distinguish among $\nu(S-S)$, $\nu(M-S_t)$ and $\nu(M-S_b)$ group present in the compound. In polysulfido complexes $\nu(S-S)$ frequencies range from ca. 400 to 600 cm^{-1}. Disulfur complexes are broadly classified into three types as shown below:
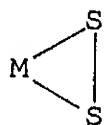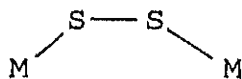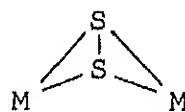
(a)   (b)   (c)

In all these complexes the $\nu(S-S)$ frequencies range from ca. 480 to 600 cm^{-1}. Comparison of the $\nu(S-S)$ values for the discrete diatomic sulfur species S_2^{3-} ($^3\Sigma_g^-$, 725 cm^{-1}),[82,83] S_2^{2-} ($^2\Pi_g$,

589 cm^{-1}),[84,85] S_2^{2-} ($^1\Sigma_g^+$, 446 cm^{-1})[86] leads to the conclusion

that the approximate charge distribution in disulfur complexes

is some where between that for S_2^- and that for S_2^{2-} . However,

there is a strong coupling of the ν(S-S) vibration with the

ν(M-S) vibrations leading to higher ν(S-S) values. This coupling

has been confirmed by observing the shift of 1-2 cm^{-1} in

ν(S-S) upon substitution of ^{92}Mo by ^{100}Mo in $[Mo_2(S_2)_6]^{2-}$ and

$[Mo_3S(S_2)_6]^{2-}$ [87-89]

The ν(M-S_n) vibrations are generally observed in the range

250 to 420 cm^{-1}. The ν(M-S_t) and ν(M-S_b) are observed in the

range 480 to 550 cm^{-1} and 430 to 460 cm^{-1}, respectively.[90-93]

The typical examples are presented in Table 1.3.

Electronic Spectra

Study of the electronic spectra of sulfido and polysul-

fido complexes of molybdenum and tungsten shows that most of

the bands in the low energy region are due to charge transfer

either from ligand to metal or metal to ligand. The longest

wavelength band in the complexes like $[MoO(S_2)(S_2CNEt_2)_2]$ is

assigned to the ligand to metal charge transfer.[94] This assign-

ment is also correct for other disulfido complexes where metal

atoms are in high oxidation state, e.g. $[Mo_2O_2(\mu\text{-}S)_2(S_2)_2]$.[36,69]

Position of the band in this region is influenced by the oxida-

tion state of the metal, metal-metal bond and also the nature

of the ligand present. However, these assignments are only

tentative and correct assignments are still open to question.

Table 1.3   Infrared Spectral Data

Compound	ν(S-S)	ν(M-S$_x$)	ν(M-S$_{term}$)	ν(M-S$_{br}$)	ν(M-O$_{term}$)	Reference
			Frequencies in cm^{-1}			
1	2	3	4	5	6	7
$Mo^{VI}OS_2(S_2CNPr_2)_2$	556	374, 350	–	–	916	94
$CpMo^{IV}(S_2)$	530	386, 351	–	–	–	95
$Mo^{V}S_2(S_2CNEt_2)_3$	555	not reported	–	–	–	42
$Mo^{VI}O_2(S_2CNEt_2)_2$	–	–	–	–	910, 877	96
$Mo_2^{V}O_2(\mu\text{-}S)_2(S_2CNEt_2)_2$	–	–	–	477, 340	967, 952	97
$Mo_2^{V}OS(\mu\text{-}S)_2(S_2CNEt_2)_2$	–	–	544	471, 337	962, 956	97
$Mo_2^{V}S_2(\mu\text{-}S)_2(S_2CNEt_2)_2$	–	–	548, 538	463, 334	–	97
$[Mo_2^{V}O_2(\mu\text{-}S)_2(S_2)_2]^{2-}$	516, 508	357, 321	–	not assigned	925	36
$[Mo_2^{V}S_2(\mu\text{-}S)_2(S_2)_2]^{2-}$	520	350	535	460	–	25
$[Mo_2^{V}OS(\mu\text{-}S)_2(S_2)_2]^{2-}$	518	350	not reported	460	940	39
$[Mo_2^{V}S_2(S_2)_6]^{2-}$	550, 551	382, 361, 354	–	–	–	38
$[Mo^{IV}S(S_2)_6]^{2-}$	544	386, 361	–	–	–	37
$[Mo^{IV}S(MoS_4)_2]^{2-}$	–	–	527	not assigned	–	40
$[Mo^{IV}O(S_4)_2]^{2-}$	not assigned	–	–	–	930	34

...contd.

Table 1.3 (contd.)

1	2	3	4	5	6	7
$[Mo^{IV}S(S_4)_2]^{2-}$	–	–	525	–	–	24
$[W_2^V S_2(\mu{-}S)_2(S_4)_2]^{2-}$	–	–	495, 506	–	–	48, 49
$[W_2^V S_2(\mu{-}S)_2(W^{VI}S_4)_2]^{2-}$	–	–	525	448, 350	–	45, 46
$[W^{IV}S(W^{VI}S_4)_2]^{2-}$	–	–	525, 490, 485	465, 435	–	40
$[W^{IV}O(W^{VI}S_4)_2]^{2-}$	–	–	495	465, 453	970	40, 43
$[W^{II}(W^{VI}S_4)_2]^{2-}$	–	–	495, 490	465, 453	–	44
$[W^{VI}S(S_2)(S_2CNEt_2)_2]$	550	–	500	–	–	42

Table 1 4 presents electronic absorption maxima for few represent-
ative examples.

X-Ray Studies

A variety of sulfido and polysulfido complexes of group
VIB elements are known and there is a continuous addition to
this. In certain cases the vibrational spectroscopy and other
conventional techniques fail to resolve the complexity of the
problem, and X-ray structure determination is the ultimate choice.
Structures of most of these complexes have been determined and
structure of few representative examples are shown in Figs. 1.1
& 1.2. Bond length of some of these complexes are given in
Table 1.5. In most of the complexes bond distances lie in the
range expected for sulfur ring.   The alteration in the S-S
bond lengths have been rationalized in terms of significant
$M(d\pi) - S(d\pi)$ interactions which perturb the $S(d\pi) - S(d\pi)$ bond-
ing between central atom.[98]

Table 1.4   Electronic absorption bands

Compounds	Colour	Band maximum (nm)	Reference
$[Mo^{VI}O(S_2)(S_2CNEt_2)_2]$	Blue	394, 581	94
$[Mo_2^{V}O_2(\mu-S)_2(S_2)_2]^{2-}$	Red orange	278, 305, 370, 463	36
$[Mo_2^{V}O_2(\mu-S)_2(S_2)_2]^{2-}$	Purple	295, 467, 573	25
$[Mo_2^{V}(S_2)_6]^{2-}$	Black green	313, 357, 417, 500, 625, 769	38, 60
$[Mo_3^{IV}S(S_2)_6]^{2-}$	Red	333, 370, 465, 541	37
$[Mo^{IV}O(S_4)_2]^{2-}$	Green	316, 475, 555	34
$[Mo^{IV}S(S_4)_2]^{2-}$	Red	316, 340, 405, 470	34
$[Mo^{IV}S(Mo^{VI}S_4)_2]^{2-}$	Dark red	270, 460	40
$[W^{VI}S(S_2)(S_2CNEt_2)_2]$	Green	602, 394, 360	42
$[W_2^{V}S_2(\mu-S)_2(W^{VI}S_4)_2]^{2-}$	Dark red	385, 294	48, 49
$[W^{IV}O(W^{VI}S_4)_2]^{2-}$	Red orange	378, 442	40
$[W^{IV}S(W^{VI}S_4)_2]^{2-}$	Golden yellow	271, 392	40

Table 1.5   Bond distances in sulfido and polysulfido complexes

Compound	(S-S) Å	(M-S$_b$) Å	M---M Å	Reference
$[Mo^{VI}OS_2(S_2CNEt_2)_2]$	2.02	-	-	94, 99
$[Mo_2^{V}O_2(\mu\text{-}S)_2(S_2)_2]^{2-}$	2.08	2.825	2.829	100
$[Mo_2^{V}OS(\mu\text{-}S)_2(S_2)_2]^{2-}$	2.063, 2.069	2.30, 2.33	2.83	39, 49
$[Mo^{IV}S(Mo^{VI}S_4)_2]^{2-}$	-	2.086	2.802, 3.082	40, 68
$[W^{VI}S(S_2)(S_2CNEt_2)_2]$	2.208	-	-	
$[W^{IV}S(W^{VI}S_4)_2]^{2-}$	-	2.07	2.882, 3.047	40, 68
$[W_2^{V}S_2(\mu\text{-}S)_2(S_2)(S_4)_2]^{2-}$	2.84	2.069, 2.117	2.84	49
$[W_2^{V}S_2(U\text{-}S)_2(S_4)_2]^{2-}$	2.083	2.321	2.834	48, 49
$[W^{III}(W^{VI}S_4)_2]^{2-}$	-	2.344	2.871	44

FIG. 1.1 CRYSTAL STRUCTURES

$[WS(S_2)(Dtc)_2]$

$[W_2S_4(WS_4)_2]^{2-}$

$[W(WS_4)_2]^{2-}$
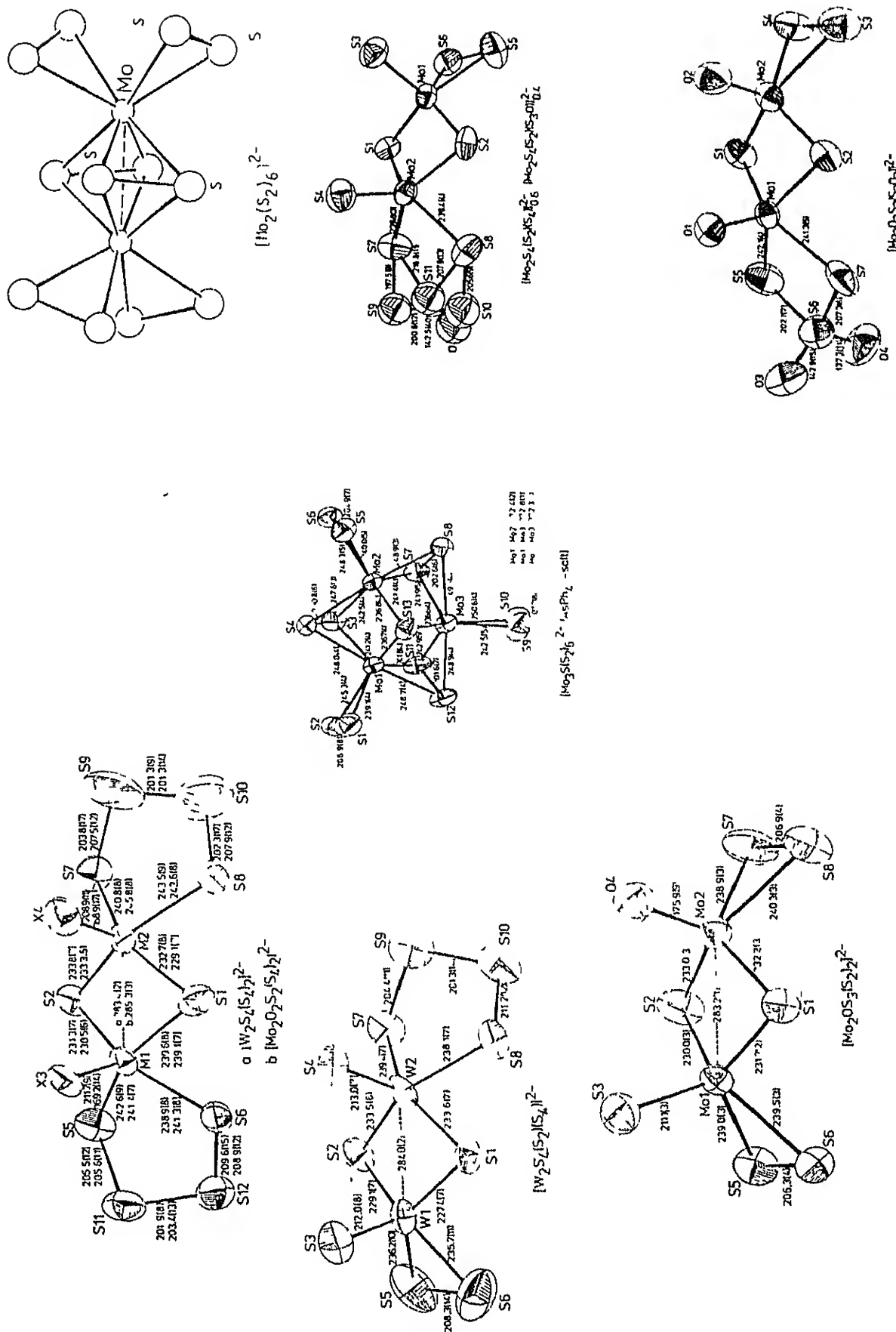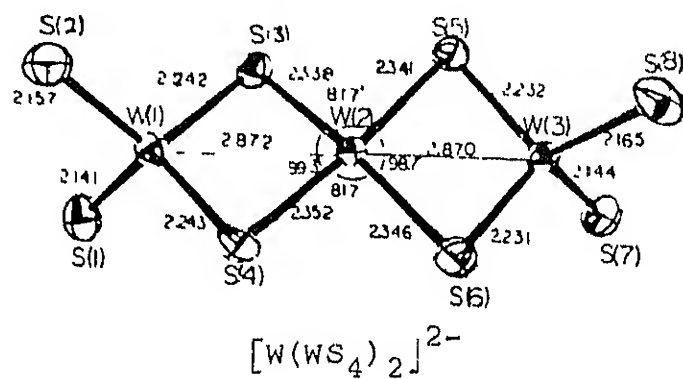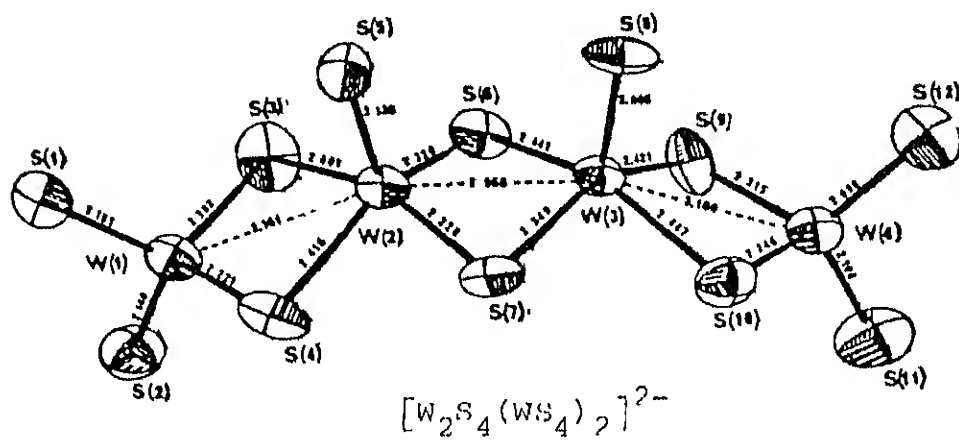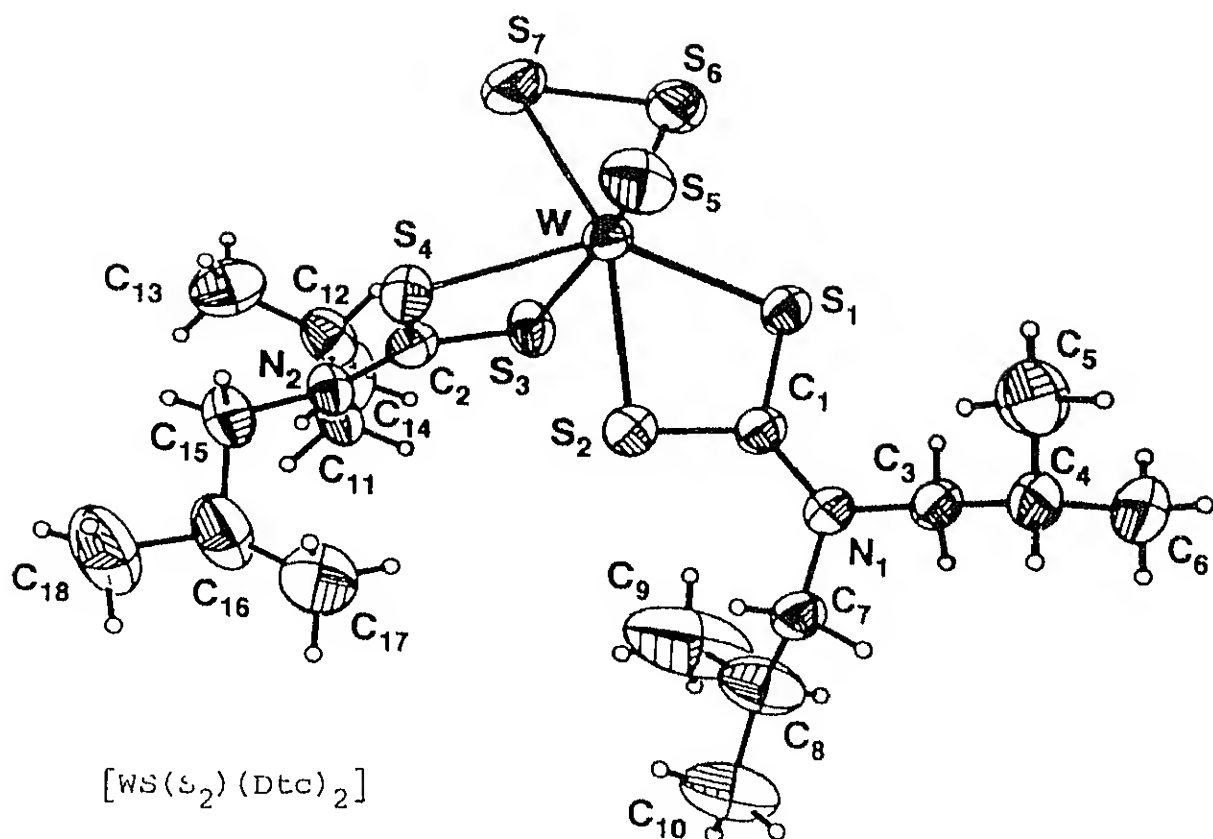
Chapter 2

SCOPE OF THE WORK

The simplest and best studied tetrathiometallates are MoS_4^{2-} and WS_4^{2-}.[102,103] First example of the intramolecular induced electron transfer in such systems is the synthesis of $[Mo_2^VO_2(\mu\text{-}S)_2(S_2)_2]^{2-}$ using oxygen as an external oxidant.[36] Another interesting reaction is the oxidation of S_x^{2-} ligand by O_2, leading to the formation of novel ligands like $S_3O_2^{2-}$ or S_3O^{2-}.[37,39] Application of this methodology to tungsten-sulfur systems is a recent phenomenon.[44,46-48] Intramolecular electron transfer across metal-sulfur bond could be extended to the corresponding tungsten systems by varying the reaction conditions. Keeping the difference between the energy levels of 5d of tungsten and 3p orbital of sulfur in consideration, an appropriate inducing source can be chosen. A broad spectrum of the inducing sources like thermal,[30,37] photochemical[32] or chemical stimuli[42] may be attempted. The variation of inducing source could be done on two counts:

i) The redox potential of the external oxidants could
be varied.

ii) Instead of one electron oxidants two electron oxi-
dants could be used.

Of the common oxidants, molecular oxygen seems to be the most
important as its role is vital in biological processes.[104] In
aprotic medium, acceptance of electrons by molecular oxygen
is a stepwise process. The first oxidation product, super-
oxide radical ion O_2^- functions as a moderate reducing agent
whereas in protic medium, the superoxide forms HO_2, a powerful
oxidant.[105] Thus the reaction conditions govern the course of
the reaction.

When two electron oxidants are used, the situation may be
a little complicated because the reaction might proceed either
through an induced electron transfer or in a purely ligand based
redox manner. To decide which one is in operation, electro-
chemical and ESR spectral studies could be helpful.
Even if the process involves induced electron transfer, there
could be two options for the reaction to proceed, either it can
take place in a concerted fashion or in a stepwise manner.
Kinetic measurements and C.V. studies can help to resolve such
problems to a greater extent.

Reactions of this type are important not only from a
mechanistic point of view but also from synthetic considerations.
Exploiting this phenomenon, new synthetic strategies can be deve-
loped for the preparation of the compounds which are not

accessible through conventional methods.

Tungsten-sulfur chemistry has invited tremendous atten-
tion in the recent years mainly because of its importance in:

i) HDS catalysis, and

ii) Biology.

HDS (hydrodesulfurization) involves the conversion of S from
crude oil fractions or coal-derived liquids in the presence of
H_2 into H_2S. Co-Mo and Ni-W units supported on alumina serve
as good catalysts.[106-110] Activation of the M-bound S_2^{2-} ligand
may be of relevance to the HDS reaction, (M = Mo, W). This
process involves the activation of H_2 and C-S bond cleavage.
The proposed mechanism for HDS reaction is shown in Scheme 2.1.[80]

This scheme is in agreement with the work of Dubois and
coworkers who demonstrated that appropriately activated S_2^{2-}
units in the $(CpMoS_2)_2$ complex are capable of activating H_2 [111]
and catalyze the reduction of elemental sulfur and hydrogenation
of alkynes.[112]

Tungsten, the only biologically active member of the 3rd
transition series plays a key role in a metalloenzyme, formate-
dehydrogenase.[101] Modelling of this enzyme, as well as some other
molybdoenzymes can be done once the synthetic strategy is deve-
loped. Most of the models proposed so far, satisfy neither the
structural nor the functional aspects of the enzymes.[94,113-116]
Hence the search for better models still continues. Some of
the molybdoenzymes retain their activity when metal center is

SCHEME 2.1

Possible Reactions of the Activated S_2^{2-} Relevant

to HDS
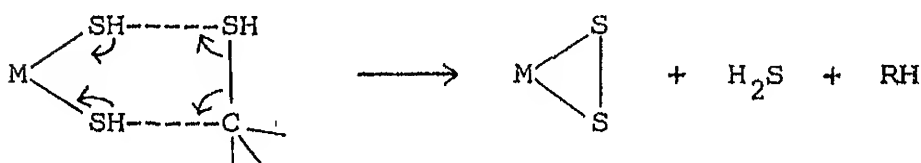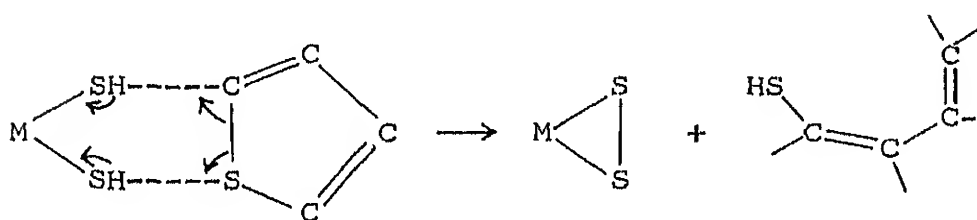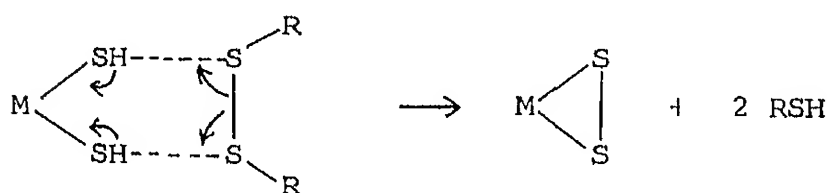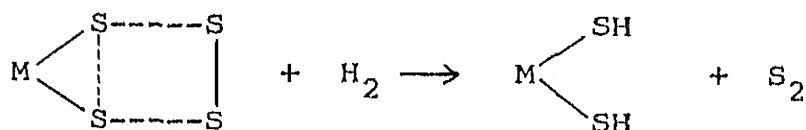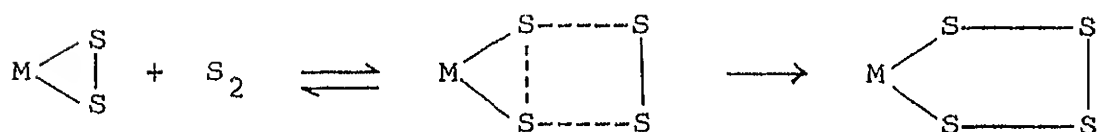
substituted by tungsten.[117,118] Thus the first step in the modelling of these enzymes could be the synthesis of a model with tungsten center. The failure in the modelling of the

molybdoenzymes lies mainly in the instability of molybdenum-sulfur systems which can serve as models whereas the corresponding tungsten compounds are generally more stable. Once these are synthesized, various aspects of the system can be studied.

Another aspect of the studies on tungsten-sulfur systems could be to see the trend in the reactivity in the series WS_4^{2-}, WOS_3^{2-} and $WO_2S_2^{2-}$ ions. Substitution of sulfur by oxygen may enhance the sluggishness of the system and a more powerful inducing agent may be needed to invoke the intramolecular electron transfer.

After successfully carrying out the work on tungstensulfur system, the feasibility of transferring the methodology to molybdenum-sulfur systems can be tried. Problems arising at this stage can be handled in two ways:

i) Nature of the inducing agent can be varied, i.e., a mild inducing agent can be used.

ii) Size of the coligand can be varied to stabilize the system.

Once the synthetic goal is achieved, the reactivity of the synthesized complexes can be explored. The general guide line to design a reaction would be parallel to molybdenum chemistry where such studies are well documented.[62-68,71-77,119-124]

Chapter 3

SYNTHESIS AND REACTIVITY OF THE COMPLEXES

General Considerations

All the reactions were carried out under dry nitrogen atmos-
phere unless otherwise specified. Solvents used were of analytical
grade and dried before use but not degassed. Dibenzoyl acétylene
and dimethyl acetylene dicarboxylate were purchased from Aldrich
and used without further purification.

3.1 Methods of Analysis and Work-up Manipulations

Elemental analyses for carbon, hydrogen and nitrogen were
done at Microanalytical Laboratory, Indian Institute of Techno-
logy, Kanpur. Sulfur was estimated as $BaSO_4$ and the procedure
employed is as follows: The complex containing sulfur (ca. 0.3 g)
was treated with an excess of alkaline bromine water. The excess
bromine was evaporated off by warming the solution slowly on a
water bath. Resulting solution was treated with HCl and the
librated bromine was again evaporated off by boiling the solution
slowly. The solution was filtered and the sulfate in the filtrate
was estimated by precipitating it as $BaSO_4$, in the usual manner.[125]

3.2 Preparation of the Starting Materials

Synthesis of $(NH_4)_2WS_4$:

H_2WO_4 (5.0 g) was treated with concentrated NH_4OH (40 ml), the slurry was saturated with H_2S at room temperature and then heated at $60^\circ C$ with stirring for 20 min. After filtration, the solution was again heated at $60^\circ C$ and H_2S bubbling continued for 8 hr. The reaction mixture was cooled to $15^\circ C$ while maintaining the H_2S flow and then the solid product was isolated by filtration, washed with i-PrOH and ether and dried in vacuo,[103,126] (yield, ∽60%). Purity of the compound was checked by electronic spectrum which shows the bands only at 393 and 277 nm (in H_2O).

Synthesis of $(NH_4)_2WOS_3$:

H_2WO_4 (5.09 g) was dissolved in a mixture of concentrated NH_4OH (20 ml) and H_2O (5 ml) and the solution was filtered. H_2S was bubbled rapidly into the solution for 15 min. at ambient temperature causing the precipitation of a minimal amount of $(NH_4)_2WO_2S_2$. The reaction mixture was filtered into ice cold i-PrOH (500 ml) and the product separated as a yellow solid which was isolated by filtration, washed with i-PrOH and ether and dried in vacuo,[126] (yield,∽ 50%).

The electronic spectrum of the compound gave characteristic bands at 375, 336, 268 and 240 nm (in H_2O).

Synthesis of $(NH_4)_2WO_2S_2$:

H_2WO_4 (5.0 g) was dissolved in a mixture of concentrated NH_4OH (20 ml) and H_2O (5 ml). The solution was filtered and placed in an ice bath. H_2S was passed rapidly over the surface of the solution for 5 min causing the separation of the yellow product which was isolated by filtration, washed with EtOH and ether and dried in vacuo,[126] (yield, ~75%).

The electronic spectrum of the compound gave characteristic bands at 326, 272, 246 nm (in H_2O).

Preparation of Methanolic Potassium Polysulfide Solution

To a mixture of potassium hydroxide (4.0 g) and sulfur (20.0 g) in methanol (100 ml), a moderately rapid stream of hydrogen sulfide was passed for two hr. The resulting orange-red solution was filtered to remove the excess sulfur and the polysulfide solution was stored in a stoppered flask.

Synthesis of $(Et_2NH_2)_2WS_4$:

Tungstic acid (5 g) was dissolved in a mixture of H_2O (10 ml) and Et_2NH (15 ml) by refluxing for 1 hr. The solution was filtered and H_2S was passed rapidly for 4 hr at 60°C. When reaction mixture was cooled, yellow crystals separated which were washed with i-PrOH and ether (yield, 7.36 g; 80%).

Anal. Calcd. for $C_8H_{24}N_2S_4W$: C, 20.86; H, 5.21; N, 6.08.

Found: C, 20.71; H, 5.42; N, 6.25%.

Synthesis of $(Et_2NH_2)_2WOS_3$:

Tungstic acid (5 g) was refluxed in a mixture of H_2O (10 ml) and Et_2NH (10 ml) for 1.5 hr, filtered, into which H_2S was bubbled rapidly for 50 min, at 60^OC. The solution was cooled and to this iso-propanol(50 ml) and ether (20 ml) were added. The yellow orange oily mass so obtained, was recrystallized from methanol/ether (yield, 6.48 g; 73%).

Anal. Calcd. for $C_8H_{24}N_2OS_3W$: C, 21.62; H, 5.40; N, 6.30.

Found: C, 20.71; H, 5.32; N, 6.28%.

Synthesis of $(Pr_2NH_2)_2WS_4$:

The same procedure was followed except the tungstic acid, water and dipropyl amine mixture was refluxed till all the tungstic acid went into the solution (yield, 63%).

Anal. Calcd. for $C_{12}H_{32}N_2S_4W$: C, 27.90; H, 6.28; N, 5.42.

Found: C, 27.72; H, 6.41; N, 5.32%

Synthesis of $(Pr_2NH_2)_2WOS_3$:

Same procedure as in the case of $(Et_2NH_2)_2WOS_3$, was followed except the tungstic acid, water, amine mixture was refluxed till all the tungstic acid went into the solution (yield, 58%).

Anal. Calcd. for $C_{12}H_{32}N_2OS_3W$: C, 28.80; H, 6.40; N, 5.60.

Found: C, 28.68; H, 6.44; N, 5.13%.

Synthesis of ($\bigcirc$NH$_2$)$_2$WS$_4$:   Same procedure as for the prepara-

tion of (Et$_2$NH$_2$)$_2$WS$_4$ was followed except the mixture of tungstic

acid, piperidine and water was refluxed till all the tungstic

acid dissolved (yield, 78%).

Anal. Calcd. for C$_{10}$H$_{24}$N$_2$S$_4$W: C, 24.79; H, 4.95; N, 5.78.

Found: C, 24.58; H, 4.78; N, 5.72%.

Synthesis of ($\bigcirc$NH$_2$)$_2$WOS$_3$:   Similar methodology was adopted as

in the case of (Et$_2$NH$_2$)$_2$WOS$_3$, except the mixture of tungstic acid,

piperidine and water was refluxed till all the tungstic acid went

into solution (yield, 61%).

Anal. Calcd. for C$_{10}$H$_{24}$N$_2$OS$_3$W : C, 25.64; H, 5.12; N, 5.98.

Found : C, 25.62; H, 5.10; N, 5.90%.

3.3.1 Induced Electron Transfer Reactions

Synthesis of (Et$_4$N)$_2$[W$_2$O$_2$(μ-S)$_2$(S$_2$)$_2$] - Method 'A'

(NH$_4$)$_2$WOS$_3$ (664 mg; 2 mmol) and Et$_4$NBr (630 mg; 3 mmol)

were dissolved in H$_2$O (20 ml) and iodine (253.8 mg; 2 mmol) was

added to it. The mixture was warmed on the water bath for 20 min,

then KOH (100 mg; 2.56 mmol) was added to it. After 5 min the

solution was filtered and the precipitate was washed with H$_2$O,

EtOH and ether and was recrystallized from CH$_3$CN/i-PrOH (yield,

180 mg; 21.12%).

Anal.Calcd. for C$_{16}$H$_{40}$N$_2$O$_2$S$_6$W$_2$: C, 22.53; H, 4.69; N, 3.28; S, 22.53.

Found: C, 22.49; H, 4.52; N, 3.08; S, 22.62%.

Synthesis of $(Et_4N)_2[W_2O_2(\mu\text{-}S)_2(S_2)_2]$ - Method 'B'

   $(NH_4)_2WOS_3$ (664 mg; 2 mmol) was dissolved in H_2O (30 ml) and solid $(NH_4)_2S_2O_8$ (228.20 mg; 1 mmol) was added shaking the solution vigorously. Solution was stirred for 4 hr and Et_4NBr (630 mg; 3 mmol) was added to it. After 10 min a 25% ammonia solution (5 ml) was added to it. This was filtered and the precipitate was washed and recrystallized as mentioned above (yield, 205 mg; ∾24%). Analysis was found to be satisfactory.

Synthesis of $(Et_4N)_2[W_2O_2(\mu\text{-}S)_2(S_2)_2]$ - Method 'C'

   $(NH_4)_2WOS_3$ (664 mg, 2 mmol) and Et_4NBr (630 mg; 3 mmol) were dissolved in DMF (20 ml) and warmed at $110^\circ C$ for 5 min. $C_6H_5\text{-}S\text{-}S\text{-}C_6H_5$ (218.34 mg; 1 mmol) or $(C_2H_5)_2N\text{-}CSSSSC\text{-}N(C_2H_5)_2$ (296.54 mg; 1 mmol) or t-butyl hydroperoxide (0.1 ml; ∾ 1 mmol) or $C_6H_5\text{-}O\text{-}O\text{-}C_6H_5$ (186.21 mg; 1 mmol) was added to it. The resulting red solution was left at $110^\circ C$ for 1/2 hr. Addition of i-PrOH (15 ml) and ether (30 ml) yielded red crystalline product which was washed with H_2O, EtOH and ether and recrystallized from CH_3CN/i-PrOH (yield, ∾70%). Analysis was found to be satisfactory.

Synthesis of $(Me_4N)_2[W_2O_2(\mu\text{-}S)_2(S_2)_2]$

   $(NH_4)_2WOS_3$ (668 mg; 2 mmol) dissolved in DMF (15 ml), Me_4NCl (219 mg; 2 mmol) dissolved in H_2O (5 ml) were mixed. This was warmed at $110^\circ C$ for 5 min and $C_6H_5\text{-}S\text{-}S\text{-}C_6H_5$ (216.34 mg; 1 mmol) was added to this solution. After 1/2 hr colour of the

solution darkened and then became orange. It was then cooled
and i-PrOH (20 ml) and ether (20 ml) was added and left for 1 hr.
The yellow product which separated out was washed with H_2O,
ethanol, and ether and recrystallized from CH_3CN/i-PrOH (yield,
426 mg; 57.56%).

Anal. Calcd. for $C_8H_{24}N_2O_2S_6W_2$: C, 12.97; H, 3.24; N, 3.78;
S, 25.94.

Found: C, 12.85; H, 3.25; N, 3.16;
S, 25.80%.

Synthesis of $(Et_4N)_2[WS(WS_4)_2]$ - Method 'A'

To a solution of $(NH_4)_2WS_4$ (1.044 g; 3 mmol) and Et_4NBr
(630 mg; 3 mmol) in H_2O (30 ml), $(NH_4)_2S_2O_8$ (228.20 mg; 1 mmol)
was added, stirring the solution vigorously. Some red precipitate
was thrown out immediately. Further stirring for 1 hr gave some
more product which was filtered, washed with EtOH and ether and
was recrystallized from CH_3CN/i-PrOH (yield, 310 mg; ∽30%).

Anal. Calcd. for $C_{16}H_{40}N_2S_9W_3$: C, 17.45; H, 3.63; N, 2.54;
S, 26.18.

Found: C, 17.52; H, 3.42; N, 2.50;
S, 26.10%.

Synthesis of $(Et_4N)_2[WS(WS_4)_2]$ - Method 'B'

$(NH_4)_2WS_4$ (1.644 g; 3 mmol) and Et_4NBr (630 mg; 3 mmol)
were dissolved in DMF (15 ml) and the solution was warmed at
$110^\circ C$ for 5 min. $(C_6H_5S)_2$ (218.34 mg; 1 mmol) was added to the
above solution with shaking. It was then cooled to room tempe-
rature. Addition of i-PrOH (20 ml) and ether (50 ml) yielded a

dark red crystalline product which was washed and recrystallized as mentioned above (yield, 605 mg; ∽58%).

Synthesis of $(Ph_4As)_2[WS(WS_4)_2]$

$(NH_4)_2WS_4$ (1.044 g; 3 mmol), $Ph_4AsCl.HCl$ (1.146 g; 2 mmol) and NaOH (80 mg; 2 mmol) were dissolved in DMF (15 ml) and warmed at $110^\circ C$ for 10 min followed by the addition of $C_6H_5-S-S-C_6H_5$ (218.34 mg; 1 mmol). On shaking colour of the solution became dark red. To the cold solution i-PrOH (20 ml) and ether (100 ml) was added. Red oily product thus obtained was repeatedly washed with EtOH and was recrystallized from CH_3CN/i-PrOH (yield, 652 mg; 39.52%).

Anal. Calcd. for $C_{48}H_{40}S_9As_2W_3$: C, 40.50; H, 2.81.

Found: C, 40.62; H, 2.48%.

Synthesis of $(Et_4N)_2[WO(WS_4)_2]$

$(NH_4)_2WS_4$ (1.044 g; 3 mmol) dissolved in DMF (15 ml) and Et_4NBr (630 mg; 3 mmol) dissolved in H_2O (5 ml) were mixed and heated at $110^\circ C$ for 15 min. To the above solution $C_6H_5-S-S-C_6H_5$ (218 mg, 1 mmol) was added and heated for a further 10 min. The resulting solution was cooled at room temperature and i-PrOH (10 ml) and ether (50 ml) were added to it.. The orange product that separated out was washed with water, EtOH and finally with ether (yield, 410 mg, ∽40%).

Analysis and spectral results are similar to that of the same compound reported earlier.[128]

Synthesis of $((PhCH_2)(C_2H_5)_3N)_2[WO(WS_4)_2]$

$(NH_4)_2WS_4$ (1.044 g; 3 mmol) dissolved in DMF (15 ml) and $[(PhCH_2)(C_2H_5)_3N]Br$ (484 mg; 2 mmol) dissolved in H_2O (5 ml) were mixed and heated at $110^\circ C$ for 10 min. followed by addition of C_6H_5-S-S-C_6H_5) (218 mg, 1 mmol) and heating for a further 10 min. To the cold solution i-PrOH (10 ml) and ether (50 ml) were added which gave oily mass. It was washed with EtOH and recrystallized from CH_3CN/i-PrOH (yield, 392 mg; 32.45%).

Anal. Calcd for $C_{26}H_{44}N_2OS_8W_3$: C, 25.82; H, 3.64; N, 2.31; S, 21.19.

Found: C, 25.77; H, 3.42; N, 2.45; S, 21.22%.

Synthesis of $((2-Cl.C_2H_4)(CH_3)_2.NH)_2[WO(WS_4)_2]$

A mixture $(NH_4)_2WS_4$ (1.044 g; 3 mmol) in DMF (15 ml) and $[(2-Cl.C_2H_4)(CH_3)_2.NH]Cl$ in H_2O (2 ml) was heated at $110^\circ C$ for five min. and C_6H_5-S-S-C_6H_5 (218.34 mg; 1 mmol) was added to it. After 1/2 hr when the colour of the solution became red, it was cooled to room temperature and i-PrOH (20 ml) and ether (40 ml) was added. An orange product separated out, which on washing with H_2O, EtOH and ether, and therafter recrystallization from CH_3CN/i-PrOH yielded 565 mg (61.08%) of the desired compound.

Anal. Calcd. for $C_8H_{22}N_2OS_8W_3$: C, 10.37; H, 2.37; N, 3.02; S, 27.66.

Found: C, 10.58; H, 2.51; N, 2.80; S, 27.52%.

3.3.2 Reactivity of the Synthesized Complexes

Reactivity of $(Et_4N)_2[W_2O_2S_6]$ with DBA or Synthesis of $(Et_4N)_2$-$[W_2O_2(\mu-S)_2(S_2C_2(COPh)_2)_2]$

Dibenzoyl acetylene (DBA) (234 mg; 1 mmol) was dissolved in CH_3CN (5 ml) and added to a solution of $[Et_4N]_2W_2O_2S_6$ (426 mg; 0.5 mmol) in CH_3CN (10 ml) and stirred for 5 min. When colour of the solution changed from orange to green, it was cooled to R.T. and EtOH was added dropwise till the solution became turbid. It was filtered and the filtrate was kept at R.T. for 2 days. Dark red needle shaped crystals separated out which were washed with EtOH and ether and dried under vacuum (yield, 130 mg; 19.7%).

Anal. Calcd. for $C_{48}H_{60}N_2O_6S_6W_2$: C, 43.63; H, 4.54; N, 2.12.

Found: C, 43.59; H, 4.52; N, 2.04%.

Reactivity of $(Et_4N)_2[W_2O_2S_6]$ with DMA or Synthesis of $(Et_4N)_2$-$[W_2O_2(\mu-S)_2(S_2C_2(COOMe)_2)_2]$

To a solution of $(Et_4N)_2[W_2O_2(\mu-S)_2(S_2)_2]$ (426 mg; 0.5 mmol) in CH_3CN (10 ml) dimethyl acetylene dicarboxylate (DMA), (0.13 ml; 1 mmol) was added and the solution was shaken well. The colour of the solution changed immediately from yellow to brown to green. After 5 hr absolute ethanol was added dropwise till it became turbid. It was left at R.T. for 2 days and the precipitate thus formed was washed with EtOH and ether and vacuum dried (yield, 230 mg; 42.91%).

Anal. Calcd. for $C_{28}H_{52}N_2O_6S_6W_2$: C, 31.34; H, 4.85; N, 2.61.

Found : C, 31.62; H, 4.76; N, 2.52%.

Synthesis of $(Et_4N)_2[W(S_2C_2(COPh)_2)_3]$

$(Et_4N)_2WS_4$ (190.6 mg; 1/3 mmol), sulfur (21.33 mg, 3/2 m-mol) and dibenzoyl acetylene (234 mg; 1 mmol) were taken in DMF (10 ml) and the solution was stirred for 12 hr. The colour of the solution changed from red to brown to greenish brown. Addition of iso-propanol till the solution became turbid, and leaving it at room temperature for 24 hr gave greenish brown crystals, which were washed with EtOH, CS_2 and ether, and dried under vacuum, yield, 165 mg (37%).

Anal. Calcd. for $C_{64}H_{70}N_2O_6S_6W$: C, 57.39; H, 5.23; N, 2.09.

Found: C, 56.65; H, 5.13; N, 1.89%.

Synthesis of $K_4[W_2O_2(\mu-S)_2(CN)_6] \cdot 3H_2O$

A suspension of $(Et_4N)_2[W_2O_2S_6]$ (852 mg; 1 mmol), potassium cyanide (2 g; 30.7 mmol) in H_2O (10 ml) was stirred for 10 min. The colour of the solution changes from green to brown and finally to bright yellow. Addition of i-PrOH (20 ml) gave some oily mass

which was recrystallized from H_2O and EtOH. Yellow crystals thus formed, were washed with ethanol and ether, and dried in vacuum; yield 600 mg (73.89%).

Anal. Calcd. for $C_6H_6N_6O_5S_2K_4W_2$: C, 8.67; H, 0.72; N, 10.12.

Found: C, 9.20; H, 0.81; N, 10.05;

3.4.1 Induced Electron Transfer Reactions Concealed Under Ligand Based Redox Processes

Synthesis of $[WO(S_2)(S_2CNEt_2)_2]$ - Method 'A'

A solution of $(Et_2NH_2)_2WOS_3$ (444 mg; 1 mmol) in DMF (10 ml) was stirred with CS_2 (2 ml) for 36 hr in the presence of air. This solution was filtered and i-PrOH (50 ml) was added to it. This was kept at room temperature for 24 hr. Brown crystalline product was thrown out, which was purified by flash chromatography on silica gel using $CHCl_3$ and petroleum ether (60:40) as eluant (yield,   390 mg;~70%).

Anal. Calcd. for $C_{10}H_{20}N_2OS_6W$: C, 21.43; H, 3.57; N, 5.00.
Found: C, 21.60; H, 3.60; N, 4.72%.

Synthesis of $[WO(S_2)(S_2CNEt_2)_2]$ - Method 'B'

$(NH_4)_2WO_2S_2$ (316 mg; 1 mmol) was dissolved in DMF (15 ml) by warming it on a hot plate. The solution was cooled and

tetraethylthiuram disulfide (296.54 mg; 1 mmol) was added to it.
The solution was filtered, and i-PrOH (10 ml), ether (200 ml) were
added to it.   Keeping the solution in the refrigerator for 4 days,
yielded brown crystalline product.   The crystals were washed with
i-PrOH, ether and dried under vacuum (yield, 55 mg (9.82%). Analy-
sis was found to be the same as in method 'A'.

Synthesis of $[WO(S_2)(S_2CNPr_2)_2]$

A solution of $(Pr_2NH_2)_2WOS_3$ (500 mg; 1 mmol) in DMF (10 ml)
was stirred with CS_2 (2.5 ml) for 40 hr in the presence of air at
room temperature.   The solution was poured into water (150 ml).
The oily material was extracted in $CHCl_3$ and was purified by flash
chromatography on silica gel using $CHCl_3$:petroleum ether mixture
(50:50) (yield, 230 mg; 37.95%) as eluant.

Anal. Calcd. for $C_{14}H_{28}N_2S_6OW$: C, 27.27; H, 4.54; N, 4.54.

Found: C, 27.10; H, 4.60; N, 4.60%.

Synthesis of $[WO(S_2)(S_2CN\bigcirc)_2]$

\ $(PipH)_2WOS_3$ (468 mg; 1 mmol) was dissolved in DMF (10 ml)
and stirred with CS_2 (3 ml) for 24 hr at room temperature. Addi-
tion of i-PrOH (10 ml) and ether (100 ml) resulted in the precipi-
tation of a brown product which was washed with H_2O, EtOH, ether
and was purified by flash chromatography using $CHCl_3$:petroleum
ether as eluant (yield, 258 mg; 44.17%).

Anal. Calcd. for $C_{12}H_{20}N_2OS_6W$: C, 24.65; H, 3.42; N, 4.79; S, 32.87.

Found: C, 24.24; H, 3.35; N, 4.60; S, 32.96%.

Synthesis of $[WS(S_2)(S_2CNEt_2)_2]$

$(Et_2NH_2)_2WS_4$ (460 mg; 1 mmol) was dissolved in DMF (10 ml) and CS_2 (2 ml) was added to it. The resultant red solution was stirred in the presence of air at room temperature for 36 hr. The solution was filtered and i-PrOH (50 ml) and ether (10 ml) were added to it. Keeping the resulting solution at $25^\circ C$ for 24 hr resulted in the separation of green crystalline product. This was washed with H_2O, EtOH, ether and dried under vacuum. The compound was purified by flash chromatography on silica gel using $CHCl_3$:petroleum ether (60:40) as eluant (yield, 282 mg; 48.92%).

Anal. Calcd. for $C_{10}H_{20}N_2S_7W$: C, 20.83; H, 3.47; N, 4.86.

Found: C, 20.86; H, 3.72; N, 4.52%.

Synthesis of $[WS(S_2)(S_2CNPr_2)_2]$

$(Pr_2NH_2)_2WS_4$ (348 mg; 1 mmol) taken in DMF (5 ml) was stirred with CS_2 (2 ml) for 48 hr. When the solution became dark green, it was poured into water (100 ml). The crude product precipitated out which was washed with H_2O, i-PrOH:ether mixture (80:20) and finally with ether. Purification by flash chromatography on silica gel using $CHCl_3$:petroleum ether (40:60) as eluant gave the

green compound (yield, 115 mg; 18.2%).

Anal. Calcd. for $C_{14}H_{28}N_2S_7W$: C, 26.58; H, 4.43; N, 4.43.

Found: C, 25.96; H, 4.46; N, 4.31%.

Synthesis of $[WS(S_2)(S_2CN\langle\quad\rangle)_2]$

(PipH)$_2$WS$_4$ taken in DMF (10 ml) was mixed with CS_2 (2 ml) and stirred vigorously for 38 hr. The solution was filtered and to the filtrate i-PrOH (10 ml) and ether (150 ml) were added to get the green crude product. It was washed with H_2O, EtOH and ether, and purified by flash chromatography using $CHCl_3$: petroleum ether (50:50) as eluant (yield, 210 mg; 35%).

Anal. Calcd. for $C_{12}H_{20}N_2S_7W$: C, 24.00; H, 3.33; N, 4.66.

Found: C, 24.21; H, 3.20; N, 4.56%.

Synthesis of $(Et_2NH_2)[WO(S_2)_2(S_2CNEt_2)]$ - Method 'A'

(Et$_2$NH$_2$)$_2$WS$_4$ (460 mg; 1 mmol) was dissolved in DMF (5 ml) and CS_2 (1 ml) was added to it. The resulting red solution was stirred for 16 hr in the presence of air. Addition of i-PrOH (50 ml) and ether (180 ml) and on keeping it at room temperature overnight resulted in the separation of reddish brown crystalline product which was washed with H_2O, i-PrOH and finally with ether and recrystallized from acetone/petroleum ether (yield, 260 mg; 47.3%).

Anal. Calcd. for $C_9H_{22}N_2OS_6W$: C, 19.63; H, 4.00; N, 5.09.

Found: C, 19.25; H, 3.75; N, 5.05%.

Synthesis of $(Et_2NH_2)[WO(S_2)_2(S_2CNEt_2)]$ – Method 'B'

$(NH_4)_2WS_4$ (348 mg; 1 mmol) was dissolved in DMF (10 ml) and heated upto 130^OC and to this tetraethylthiuram disulfide (296.54 mg; 1 mmol) was added. The solution was cooled to room temperature. To this iso-propanol (20 ml) and ether (150 ml) were added. Further cooling of the resultant solution to 5^OC and keeping it at the same temperature for 24 hr gave reddish brown crystalline product along-with microcrystalline red product. The reddish brown product was extracted in acetone (20 ml) and was precipitated by adding petro-leum ether (20 ml) (yield, 60 mg; 10.9%). The analytical data was identical with that of the compound obtained from method 'A'.

Synthesis of $(Pr_2NH_2)[WO(S_2)_2(S_2CNPr_2)]$

$(Pr_2NH_2)_2WS_4$ (516 mg; 1 mmol), was dissolved in DMF (5 ml) and CS_2 (1 ml) was added to it. Resultant red solution was stirr-ed for 24 hr. Addition of iso-propanol (10 ml) and ether (200 ml) and keeping the solution mixture for 3 days yielded dark brown needle shaped crystals which were washed with iso-propanol:ether mixture (50:50) and then finally with ether (yield, 90 mg; 14.85%).

Anal. Calcd. for $C_{13}H_{30}N_2S_6OW$: C, 25.74; H, 4.94; N, 4.62.

Found: C, 25.62; H, 5.00; N, 4.51%.

3.4.2 Reactivity of the Synthesized Complexes

Reactivity of $[WO(S_2)(S_2CNEt_2)_2]$ with KCN or Synthesis of
$[WO(S_2CNEt_2)_2]$

$[WO(S_2)(S_2CNEt_2)_2]$ (280 mg; 0.5 mmol) was dissolved in dichloromethane (10 ml) and KCN (65 mg; 1 mmol) was dissolved in H_2O (5 ml) and EtOH (5 ml). Both the solutions were mixed and stirred vigorously for 6 hr. Partial evaporation of the solution gave a white crystalline product. The crystals were washed with H_2O and dried under vacuum (yield, 90 mg; 36.29%).

Anal. Calcd for $C_{10}H_{20}N_2OS_4W$: C, 24.19; H, 4.03; N, 5.64.

Found: C, 24.10; H, 3.72; N, 5.56%.

Reactivity of $[WO(S_2)(S_2CN⬡)_2]$ with KCN or Synthesis of
$[WO(S_2CN⬡)_2]$

$[WO(S_2)(S_2CN⬡)_2]$ (292 mg; 0.5 mmol) dissolved in dichloromethane (10 ml) and KCN (65 mg; 1 mmol) dissolved in H_2O (5 ml) and EtOH (5 ml) were mixed and stirred vigorously for 6 hr. Partial evaporation of the solution gave white crystalline product. The product was washed well with H_2O and dried under vacuum (yield, 110 mg; ∽ 42%).

Anal. Calcd. for $C_{12}H_{20}N_2OS_4W$: C, 27.69; H, 3.84; N, 5.38.

Found: C, 27.80; H, 3.73; N, 5.22%.

Reaction of $[WO(S_2CNEt_2)_2]$ with Elemental Sulfur

$[WO(S_2CNEt_2)_2]$ (496 mg; 1 mmol) was dissolved in acetone and sulfur (64 mg; 2 mmol) was added to it. Solution mixture was refluxed for 10 hr and solvents were evaporated. The solid so obtained was recrystallized from $CHCl_3$/pet. ether. The compound gave satisfactory analytical results for $[WO(S_2)(S_2CNEt_2)_2]$ (vide supra).

Reaction of $[WO(S_2)(S_2CNEt_2)_2]$ with PhSH

$[WO(S_2)(S_2CNEt_2)_2]$ (560 mg; 1 mmol) was dissolved in CH_2Cl_2 and PhSH (0.2 ml ; 2 mmol) was added. The solution was stirred for 20 hr. Addition of Et OH (20 ml) resulted in the separation of yellow precipitate. This was washed with Et OH and ether and then recrystallized from CH_2Cl_2/pet.ether. On the basis of spectral and elemental analysis, the product was identified as $[W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (vide infra).

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3.5.1 Thermally Induced Electron Transfer Reactions

Synthesis of $[W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ – Method 'A'

To a solution of $(Et_2NH_2)_2WOS_3$ (888 mg; 2 mmol) in DMF (10 ml), CS_2 (2 ml) was added and the mixture was refluxed for 4 hr. Addition of i-PrOH (10 ml) and ether (100 ml) to the cold solution, precipitated a small amount of green brown product which was filtered off and the filtrate was kept overnight at room temperature to yield the desired compound as yellow needles. The

compound was washed with H_2O, EtOH and ether and purified chromatographically using CH_2Cl_2/pet. ether (80:20) as eluant (yield, 290 mg; 38%).

Anal. Calcd. for $C_{10}H_{20}N_2O_2S_6W_2$: C, 15.78; H, 2.63; N, 3.68.

Found : C, 15.90; H, 2.81; N, 3.48%.

Synthesis of $[W_2O_2(\mu S)_2(S_2CNEt_2)_2]$ – Method 'B'

To a hot solution (130°C) of $(NH_4)_2WO_2S_2$ (632 mg; 2 mmol) in DMF (10 ml) tetraethylthiuram disulfide (296 mg; 1 mmol) dissolved in DMF (5 ml) was added and the solution was cooled to 25°C. Addition of i-PrOH (20 ml) and ether (160 ml) and keeping it at 5°C for 48 hr, yielded yellow product which was purified as described above (yield, 340 mg; ∽45%).

Synthesis of $[W_2O_2(\mu\text{-}S)_2(S_2CN\langle\bigcirc\rangle)_2]$

To a hot solution (130°C) of $(NH_4)_2WO_2S_2$ (632 mg; 2 mmol) in DMF (15 ml), dicyclopentamethylenethiuram disulfide (320.6 mg; 1 mmol) dissolved in DMF (5 ml) was added. The solution was cooled immediately to room temperature and i-PrOH (15 ml) and ether (150 ml) were added to it. Keeping the solution at 5°C for 24 hr yielded a yellow powder which was washed with H_2O, EtOH and ether and purified chromatographically using CH_2Cl_2/pet. ether (70:30) as eluant (yield, 180 mg; ∽23%).

Anal. Calcd. for $C_{12}H_{20}N_2O_2S_6W_2$: C, 18.36; H, 2.55; N, 3.57.

Found : C, 18.50; H, 2.44; N, 3.21%.

Synthesis of $[W_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ - Method 'A'

A solution of $(Et_2NH_2)WS_4$ (920 mg; 2 mmol) DMF (10 ml) and CS_2 (2 ml) was refluxed for 4 hr under dry nitrogen atmosphere and in the absence of light. To the cold solution ($25^{\circ}C$), i-PrOH (10 ml) and ether (100 ml) were added. A small amount of dark brown product precipitated out which was filtered off. The filtrate was left at room temperature for 24 hr to yield the desired compound as dark red needle shaped crystals. The compound was washed with H_2O, EtOH and ether and purified chromatographically using CH_2Cl_2/pet. ether (75:25) as eluant (yield 220 mg; 28%).

Anal. Calcd. for $C_{10}H_{20}N_2S_8W_2$: C, 15.15; H, 2.52; N, 3.53.
Found: C, 15.45; H, 2.40; N, 3.68%.

Synthesis of $[W_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ - Method 'B'

Tetraethylthiuram disulfide (296 mg; 1 mmol) dissolved in DMF (5 ml) was added to a solution of $(NH_4)_2WS_4$ (696 mg; 2 mmol) in DMF (10 ml) at $130^{\circ}C$ under dry nitrogen atmosphere. To the cold solution ($25^{\circ}C$) i-PrOH (10 ml) and ether (250 ml) were added and kept at $5^{\circ}C$ for 25 hr. The crude product thus obtained was washed and purified as described above (yield, 96 mg; 12%). Analysis was found to be satisfactory.

Synthesis of $[W_2OS(\mu\text{-}S)_2(S_2CNEt_2)_2]$

The same procedure as for the preparation of $[W_2S_2(\mu\text{-}S)_2$ $(S_2CNEt_2)_2]$ (method A) was followed except that the reaction was

carried out in the presence of air. The desired compound was obtained as major product (234 mg; ∽30%) after chromatographic purification. However, if method B synthesis of $[W_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ is followed in the presence of air, the desired product is obtained in low yield (90 mg; ∽12%).

Anal. Calcd. for $C_{10}H_{20}N_2OS_3W_2$: C, 15.46; H, 2.57; N, 3.60.

Found: C, 15.78; H, 2.50; N, 3.72%.

Synthesis of $[W_2OS(\mu\text{-}S)_2(S_2CN\langle\hexagon\rangle)_2]$

$(NH_4)_2WS_4$ (696 mg; 2 mmol) was dissolved in DMF (10 ml) and heated in the presence of air at 130°C for 2 min. Dicyclopenta-methylenethiuram disulfide (320.6 mg; 1 mmol) was dissolved in DMF (5 ml). Both the solutions were mixed and cooled to room temperature immediately. Addition of i-PrOH (20 ml) and ether (150 ml) and keeping at 5°C for 24 hr yielded an orange product which was purified chromatographically using CH_2Cl_2/pet.ether (75:25) as eluant (yield, 180 mg; ∽23%).

Anal. Calcd. for $C_{12}H_{20}N_2OS_7W$: C, 18.00; H, 2.50; N, 3.50.

Found: C, 19.63; H, 2.46; N, 3.46%.

Disproportionation Reaction of $[WO(S_2)(S_2CNEt_2)_2]$ or Synthesis of $[W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ by Thermal Induction

$[WO(S_2)(S_2CNEt_2)_2]$ (560 mg; 1 mmol) was dissolved in DMF (10 ml) and warmed on a water bath for 1 hr. The colour of the solution faded from brown to yellow. The yellow compound was

isolated by precipitating it by adding i-PrOH (20 ml) and ether (200 ml) to the solution and recrystallizing from CH_2Cl_2/pet.ether (yield, 265 mg; ∼70%).

Disproportionation Reaction of $(Et_2NH_2)[WO(S_2)_2(S_2CNEt_2)]$ or Synthesis of $[W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ by Thermal Induction

$(Et_2NH_2)[WO(S_2)_2(S_2CNEt_2)]$ (550 mg; 1 mmol) was dissolved in DMSO (10 ml) and warmed on a water bath for 30 min. The colour of the solution changed from red brown to yellow. The reaction mixture was poured into water (100 ml). The solid obtained was filtered, washed with EtOH, CS_2 and ether, dried and recrystallized from CH_2Cl_2/pet. ether. The compound thus obtained gave satisfactory elemental analysis.

3.5.2 Reactivity of the Synthesized Complex

Reaction of $[W_2OS(\mu\text{-}S)_2(S_2CNEt_2)_2]$ with KCN

A suspension of $[W_2OS(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (776 mg; 1 mmol), KCN (65 mg; 1 mmol) and Et_4NBr (210 mg; 1 mmol) in $CHCl_3$ (50 ml), EtOH (15 ml) and H_2O (5 ml) was refluxed for 96 hr. The solvents were evaporated and the residue was washed with H_2O, MeOH and ether. The bright yellow powder was dried and recrystallized from CH_2Cl_2/pet. ether. The compound gave elemental analysis and spectral results identical to that of $[W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$. The aqueous extract gave a positive test for the presence of SCN^-.

Chapter 4

RESULTS AND DISCUSSION

Physical Measurements

Infrared spectra

   Infrared spectra of the samples were recorded on a Perkin-
Elmer Model-580 infrared grating spectrophotometer. Samples were
prepared as CsI pellets and referenced to polystyrene bands.

Electronic spectra

   Electronic spectra were recorded on Cary 17D and Shimadzu
UV-190 double beam spectrophotometer using matched quartz cells.

NMR spectra

   ^{1}H NMR spectra were taken on Varian EM-390, 90 MHz spectro-
meter and ^{13}C NMR spectra were recorded on Varian CFT-20 400 MHz
spectrometer.

ESR Spectra

Electron spin resonance spectra were obtained on a Varian E-109 EPR system (X-band) using DPPH as calibrant.

C.V. Studies

Voltammetric measurements were done on PAR model 370-4 electrochemistry system: 174-A, polarographic analyzer; 175, Universal programmer; RE0074, XY recorder. All experiments were done under dinitrogen atmosphere in a three-electrode configuration using platinum and glassy-carbon working electrodes in +ve and -ve potential region. All results were collected at 298 K and referenced to a saturated calomel electrode (SCE). The reported results are uncorrected for junction contribution.

X-Ray Studies

X-ray diffractograms were taken on Siefert ISO-DEBYFLEX X-200 diffractometer using Cu-K$_\alpha$ as radiation source. Samples were fixed on an aluminium plancket. XPS measurements were carried out on ESCALAB 510 photoelectron spectrometer using the Al-K$_\alpha$ line (1486.6 e.V.) radiation.* X-ray structure of (Et_2NH_2)-$[WO(S_2)_2(S_2CNEt_2)]$ was solved by conventional heavy-atom methods.* Diffraction data were collected using Syntex P2$_1$-diffractometer (ω-scan, at 21°C).

4.1 Redox Based Synthetic Aspects of the Present Work

The electronic spectrum of WS_4^{2-} shows the lowest energy charge transfer band at 393 nm.[126] The corresponding absorption

*Courtesy, Professor A. Müller, Bielefeld, W.G.

for MoS_4^{2-} is at 467 nm. This difference in absorption may be taken as a qualitative guideline to understand any difference in the reactivity of these thiometallates when electron transfer react-ions are under consideration. Intramolecular electron transfer across W-S bond may be schematically shown as follows:
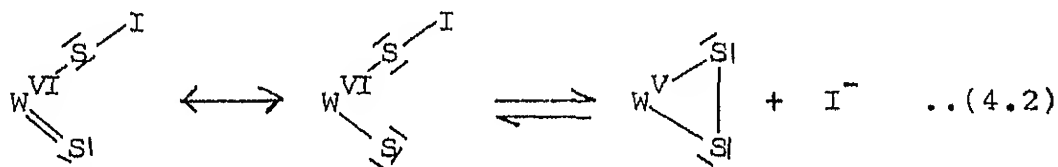
$$
\underset{\substack{(n^+)\ 2S^{2-}\\(a)}}{W{\overset{S}{\underset{S}{<}}}}
\longleftrightarrow
\underset{\substack{(n^+)\ (2S^{2-})\\(b)}}{W{\overset{/S/}{\underset{\backslash S\backslash}{<}}}}
\rightleftharpoons
\underset{\substack{(n-2)(S_2{}^{2-})\\(c)}}{W{\overset{S|}{\underset{S|}{<}}}}
\rightleftharpoons
\underset{\substack{(n-4)^+\\(d)}}{W}
\ +\
\underset{(S_2)^0}{{\overset{/S\backslash}{\underset{\backslash S/}{\|}}}}
\qquad ..\ (4.1)
$$
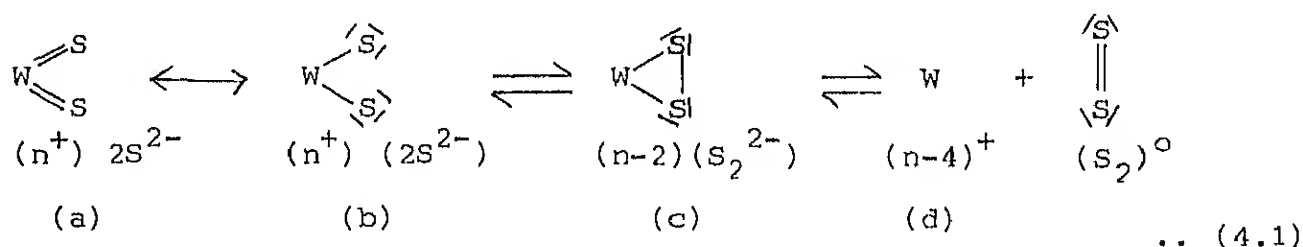
Structures (4.1a) and (4.1b) simply show the resonating forms of the tungsten sulfide attachment. The structure 4.1b is attained under the extreme reaction conditions imposed on the system. This could be achieved by several means (_vide_ _supra_). This form is ready to interact with the external oxidant. Electrophilic attack by iodine might give the intermediate like $\left[W{\overset{\overline{S}-I}{\underset{\overline{S}|}{<}}}\right]$. The energy level of this intermediate could change in such a manner that the frontier orbitals related to tungsten and sulfur might come close in energy and the electron transfer from sulfur to tungsten followed by sulfur-sulfur bond formation might take place. The formation of disulfide is reminiscent of the reaction of iodine with RS^- to form R-S-S-R. The process can be viewed as follows:

$$
W{\overset{VI}{{\overset{/S-I}{\underset{\backslash S|}{<}}}}}
\longleftrightarrow
W{\overset{VI}{{\overset{/S-I}{\underset{\backslash S/}{<}}}}}
\rightleftharpoons
W{\overset{V}{{\overset{/S|}{\underset{\backslash S|}{<}}}}}
\ +\ I^-
\qquad ..(4.2)
$$

If this happens to be the cause of the reaction occurring, an intermediate, monomeric, pentavalent tungsten species could be identified in the progress of the reaction, if not isolable. The intermediate pentavalent species arising from WOS_3^{2-} might have the structure:
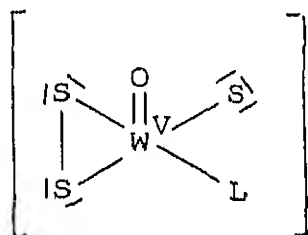
The coordination of the solvent (L) in this structure is in confirmation with the known stable pentavalent complexes of molybdenum and tungsten.[113-116,129] The presence of an intermediate, monomeric species of this type has been shown by E.S.R. spectroscopy (vide infra). This species might dimerise to give the desired product as shown below:

$$2\ W^{VI}OS_3^{2-} + I_2 \xrightarrow{\ \ L\ \ } 2\left[\ \right]^- + 2\ I^- \qquad ..(4.3)$$
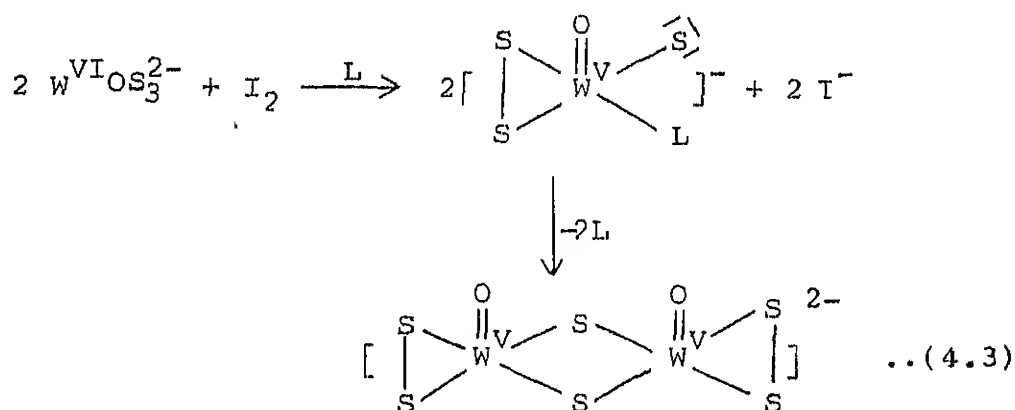
Overall process involved is the 4 e^- oxidation of 4 S^{2-} coordinated to W(VI), and the formation of two S_2^{2-} ligands. Out of

four electrons generated, the two go to external oxidant $2 \ I^O$ to produce $2 \ I^-$ and the remaining two go, one each, to the two $W(VI)$ (internal oxidant) to produce two $W(V)$, as shown below:

$$4 \ S^{2-} \longrightarrow 2 \ S_2^{2-} + 4 \ e^-$$

$$2 \ I^O + 2 \ e^- \longrightarrow 2 \ I^-$$

$$2 \ W(VI) + 2 \ e^- \longrightarrow 2 \ W(V)$$
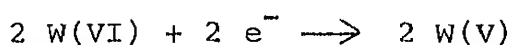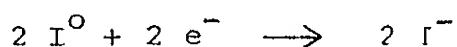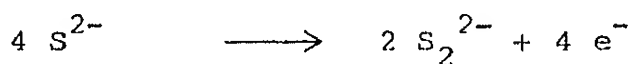
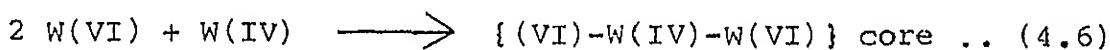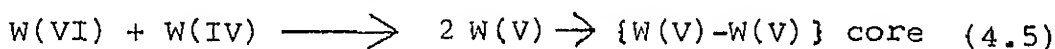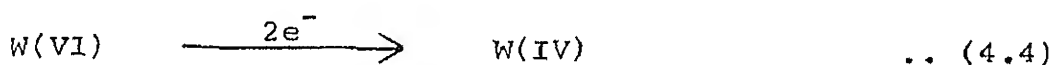Sometimes the rate of addition of the external oxidant, concentration of the reactants and the presence of counter ion govern the course of the reaction. Thus, the isolation of $[W^{IV}S(W^{VI}S_4)_2]^{2-}$ directly suggests that the generation of $W(IV)$ species takes place directly presumably by the acceptance of two electrons by $W(VI)$ center and the excess WS_4^{2-} functions as bidentate ligand, competing with any S_2^{2-} ligands formed in the reaction. Presence of bulky cation freezes the reaction at this point and the formation of trinuclear species is achieved. When two electron oxidants are used, both the products can be obtained depending upon the reaction conditions. There is no apparent difference in the inducing reactivity of the external oxidants $Ph-S-S-Ph$, $(CH_3)_3COOH$, or $Ph-CH_2-O-O-CH_2-Ph$. However, when persulfate $S_2O_8^{2-}$ is used, reaction takes place at low temperature.

As stated earlier, reaction time is also crucial in such systems, prolonging the reaction results in the formation of dinuclear species having $W(V)$ center. This suggests that the other possible electron transfer pathway could be similar to that of the
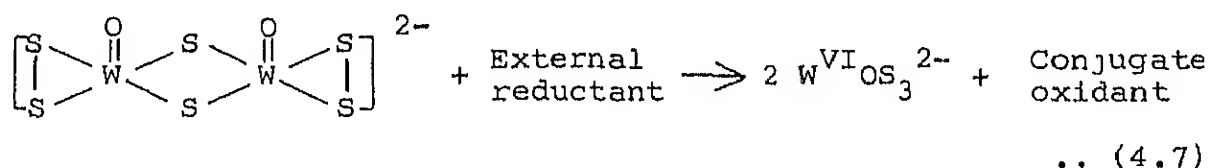
scheme proposed by Muller and later by Stiefel and coworkers[36,40] in the synthesis of $[Mo_2{}^VO_2(\mu-s)_2(S_2)_2]^{2-}$ and $[M^{IV}S(M^{VI}S_4)_2]^{2-}$, (M = Mo, W). The other possible scheme can be described as shown below:

$$W(VI) \xrightarrow{\quad 2e^-\quad} W(IV) \qquad\qquad\qquad .. (4.4)$$

$$W(VI) + W(IV) \longrightarrow 2\ W(V) \rightarrow \{W(V)-W(V)\}\ \text{core} \quad (4.5)$$

$$2\ W(VI) + W(IV) \longrightarrow \{(VI)-W(IV)-W(VI)\}\ \text{core} \quad .. (4.6)$$

The formation of $[W_2{}^VO_2(\mu-s)_2(S_2)_2]^{2-}$ in aqueous medium using persulfate as an oxidizing agent shows the dependence of the reaction on the counter ion to determine the course of the reaction. If the bulky cation is not added in the beginning, along with $[W_2O_2(\mu-s)_2(S_2)_2]^{2-}$ another species containing $\{W_2{}^VO_2(\mu-s)_2\}^{2+}$ core is obtained which has $WS_4{}^{2-}$ instead of $S_2{}^{2-}$ as bidentate ligands.[131] Contrary to molybdenum system the reaction of $WS_4{}^{2-}$ and persulfate does not yield $[W_3{}^{IV}(S)(S_2)_6]^{2-}$ anion. This may be attributed to the instability of $[W_2{}^VO_2(\mu-s)_2(S_2)_2]^{2-}$ in solution. Further reduction of W centers leads to the total decomposition of the complex.
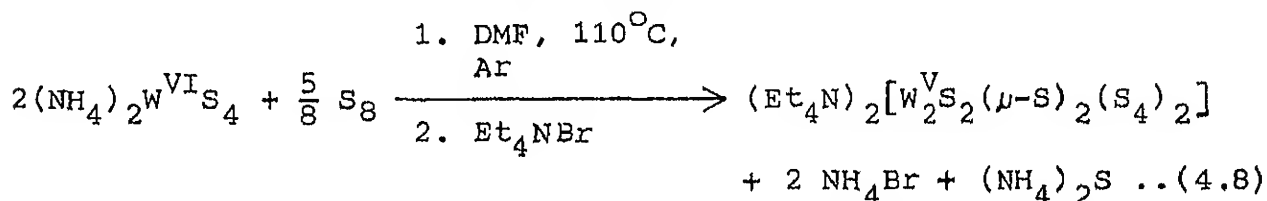
Interestingly, the reaction of $[W_2{}^VO_2(\mu-s)_2(S_2)_2]^{2-}$ and methanolic polysulfide solution at ambient conditions produces $W^{VI}OS_3{}^{2-}$ which suggests the involvement of a complimentary reaction. Here an induced electron transfer process takes place in a reverse direction. Polysulfide, $S_x{}^{2-}$ functions as an external

reductant and causes the electron transfer from metal, W(V) to coordinated ligand $S_2{}^{2-}$. Conversion of two $S_2{}^{2-}$ to 4 S^{2-} requires four electrons. Two electrons are supplied by internal reductant 2 W(V) and the rest two electrons are supplied by external reductant $S_x{}^{2-}$. The nature of the reaction has been established as shown in Eqn. (4.7):

$$\left[\begin{array}{c} S \\ S \end{array}\!\!>\!\!\overset{\overset{O}{\|}}{W}\!\!<\!\!\overset{S}{\underset{S}{}}\!\!>\!\!\overset{\overset{O}{\|}}{W}\!\!<\!\!\begin{array}{c} S \\ S \end{array}\right]^{2-} + \begin{array}{c}\text{External}\\\text{reductant}\end{array} \longrightarrow 2\ W^{VI}OS_3{}^{2-} + \begin{array}{c}\text{Conjugate}\\\text{oxidant}\end{array}$$

.. (4.7)

When a DMF solution of $\left[W_2{}^V O_2(\mu\text{-S})_2(S_2)_2\right]^{2-}$ is treated with methanolic polysulfide solution, there is immediate drop in the extinction coefficient of the bands responsible for this core. If this mixture is slightly warmed, the reaction becomes faster and quantitative conversion of $\left[W_2{}^2 O_2(\mu\text{-S})_2(S_2)_2\right]^{2-}$ to $WOS_3{}^{2-}$ is achieved.

The above mentioned complimentary reaction has also been observed by Stiefel and coworkers in the synthesis of $\left[W_2{}^V S_2(\mu\text{-S})_2(S_4)_2\right]^{2-}$. The following reaction proceeds only under a strong jet of argon gas on the surface of the reaction mixture. If reaction conditions are not standardized W(VI) species are also obtained along with the product.
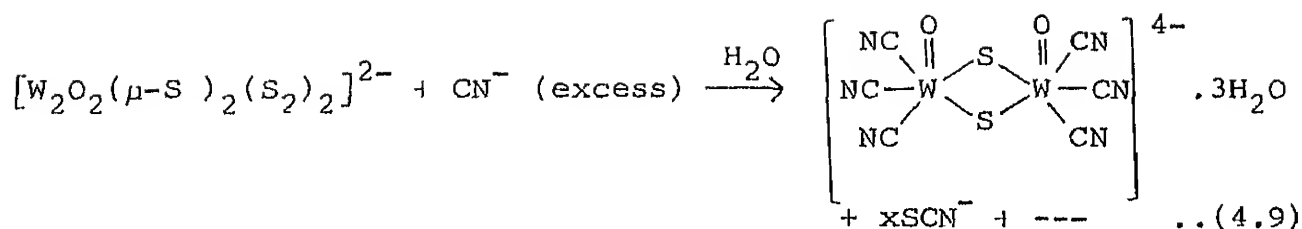
$$2(NH_4)_2 W^{VI}S_4 + \tfrac{5}{8}\,S_8 \xrightarrow[\text{2. Et}_4\text{NBr}]{\text{1. DMF, }110^{O}\text{C, Ar}} (Et_4N)_2\left[W_2^V S_2(\mu\text{-S})_2(S_4)_2\right]$$

$$+ 2\ NH_4Br + (NH_4)_2S \quad ..(4.8)$$

In this case one of the byproducts, $(NH_4)_2S$ might combine with elemental sulfur to form ammonium polysulfide which in turn might react with $[W_2^VS_2(\mu-S)_2(S_4)_2]^{2-}$ in a complimentary fashion, pushing the equilibrium in the backward direction, thereby forming WS_4^{2-}. Thus, the role of the argon jet is to remove byproduct $(NH_4)_2S$ and to push the reaction in the forward direction.[48]

Formation of MoS_9^{2-} from MoS_4^{2-} and elemental sulfur (external oxidant) is readily achieved whereas under similar reaction conditions $W S_9^{2-}$ is not formed. This clearly shows the difference in reactivity between these two thiometallates, MoS_4^{2-} and WS_4^{2-} anions. However, molybdenum analog of $[W_2^VO_2(\mu-S)_2(S_2)_2]^{2-}$ is formed under mild condition.[48] This suggests that the anion WS_9^{2-} might exist in solution if not isolable. This species has not been isolated so far, however, it has been shown by Coucouvanis and coworkers that MoS_9^{2-} reacts readily with activated acetylene to yield the tris-dithiolene chelate $[Mo^{IV}(S_2C_2-(COOMe)_2)_3]^{2-}$.[76] In this reaction the oxidation state of the central metal atom remains unchanged. Similar dithiolene complexes of Mo and W have been synthesized by Stiefel and coworkers where no apparent redox chemistry is involved. However, we have observed that the reaction between WS_4^{2-} and dibenzoyl acetylene in the presence of elemental sulfur yields, a tris-dithiolene complex anion $[W^{IV}(S_2C_2(COPh)_2)_3]^{2-}$. Same results were obtained when MoS_4^{2-} anion is used in place of WS_4^{2-} anion.[133] Thus, it may be inferred that WS_4^{2-} and elemental sulfur does give a reactive intermediate very much similar to MoS_9^{2-} which in turn reacts with the activated acetylene to

produce the monomeric tris-dithiolene complex of W(IV).

Recently, an interesting reaction between $[Mo_2{}^VO_2(\mu-S)_2-(S_2)_2]^{2-}$ and activated acetylene has been shown where insertion has taken place across Mo-S bond with the formation of vinyl disulfide group.[78] Coucouvanis and coworkers in a series of reaction have shown that there is a distinct difference in the reactivity between $S_2{}^{2-}$ and $S_4{}^{2-}$ ligands coordinated to molybdenum systems.[79] They have suggested that sometimes insertion of the above type might take place at ambient temperature which on refluxing at higher temperature changes to stable dithiolene isomer.[79,80] The reaction between $[W_2{}^VO_2(\mu-S_2)(S_2)_2]^{2-}$ and dibenzoyl acetylene (DBA) at room temperature gives the dithiolene product $[W_2{}^VO_2(\mu-S_2)_2(S_2C_2(\text{COPh})_2)_2]^{2-}$ instead of forming vinyl disulfide ligand as has been observed in the corresponding molybdenum analog. This reaction is expected from symmetry consideration contrary to molybdenum reaction.[80] However, the cleavage of S-S bond in coordinated $S_2{}^{2-}$ even at ambient temperature is suggestive of instability of $W{\Big\langle}{\overset{\displaystyle S}{\underset{\displaystyle S}{|}}}$ moiety compared to $Mo{\Big\langle}{\overset{\displaystyle S}{\underset{\displaystyle S}{|}}}$ (vide infra).

The difference in reactivity between $[Mo_2{}^VO_2(\mu-S)_2(S_2)_2]^{2-}$ and $[W_2{}^VO_2(\mu-S_2)(S_2)_2]^{2-}$ is further reflected in a reaction of these two anions with KCN. Contrary to molybdenum system[133] where reduction of molybdenum centers takes place, the tungsten system shows a simple substitution reaction with the formation of $[W_2{}^VO_2(\mu-S)_2(CN)_6]^{4-}$ as shown below:

$$[W_2O_2(\mu-S)_2(S_2)_2]^{2-} + CN^- \text{ (excess)} \xrightarrow{H_2O} \begin{bmatrix} \text{NC} \overset{O}{\underset{}{\parallel}} S \overset{O}{\underset{}{\parallel}} \text{CN} \\ \text{NC}-W W-\text{CN} \\ \text{NC} S \text{CN} \end{bmatrix}^{4-} .3H_2O$$

$$+ xSCN^- + --- \qquad ..(4.9)$$

The reactivity of $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ has also been checked with CS_2. No reaction takes place even on refluxing the two for hours.

The reaction between $(R_2NH_2)_2WOS_3$ and CS_2 in the presence of oxygen gives $[W^{VI}O(S_2)(S_2CNEt_2)_2]$. This reaction is actually an induced electron transfer reaction but paradoxically seems to be similar to a purely ligand redox process. The stoichiometry of this reaction has been established as shown in reaction (4.10).

$$(R_2NH_2)_2W^{VI}OS_3 + 2 \ CS_2 + \frac{1}{2} O_2 \longrightarrow [W^{VI}O(S_2)(S_2CNR_2)_2]$$

$$+ H_2S + H_2O \qquad .. (4.10)$$
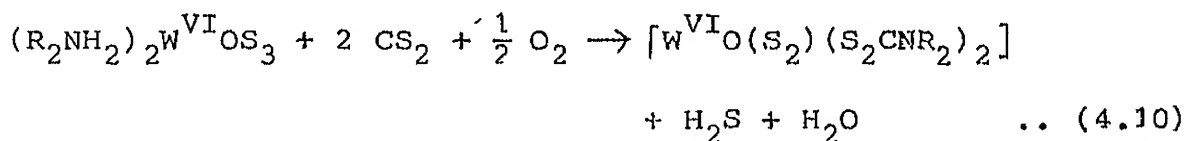
$R_2NH = Et_2NH, \ Pr_2NH, \ \langle\bigcirc\rangle NH.$

The formation of $[W^{VI}S(S_2)(S_2CNR_2)_2]$ can also be effected following the reaction (4.10) using the corresponding salt of tetrathiotungstate(VI). This product is similar to the one formed by reacting WS_4^{2-} and tetraalkylthiuram disulfide as

oxidant.[134] The difference lies in the type of reaction involved herein. The latter reaction is a purely ligand based redox process whereas reaction (4.10) involves the participation of tungsten.
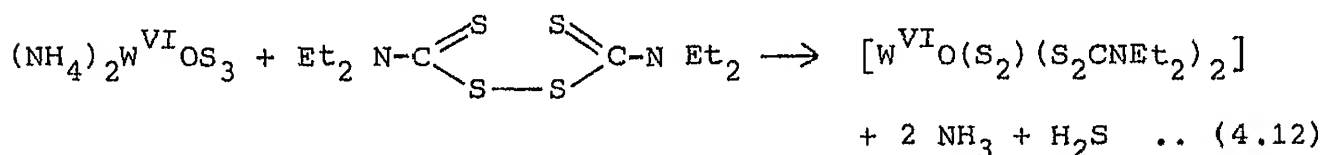
The product of the reaction (4.10) maintains hexavalent tungsten apparently suggesting a purely ligand redox reaction. The conversion of two S^{2-} ligands to one S_2^{2-} ligand and the uptake of two electrons by $\frac{1}{2} O_2$ as electron acceptor furnishes an electron balanced reaction. The participation of tungsten in this reaction is observed as an intermediate ESR active $W(V)$ species formed during the course of the reaction (vide infra). The observed reactions do not take place if the reaction is carried out exclusively in an inert or H_2S atmosphere. This rules out the possibility of the involvement of H^+ as an alternative electron acceptor. The disappearance of the ESR active species after 20 hr might be due to (1) further reduction of $W(V)$ to $W(IV)$, (2) oxidation of $W(V)$ to $W(VI)$ or (3) dimerization of $W(V)$. The third possibility can be ruled out as no dimeric $W(V)$ compound could be isolated under the reaction conditions within 40 hr. Second possibility, i.e. the oxidation of $W(V)$ to $W(VI)$ should lead to the formation of the product. Freezing of the reaction at this stage gives the product in low yield ($\sim 30\%$). Thus to increase the formation of the product in more than two fold from this stage, the last 16 hr are crucial when the reaction mixture is ESR silent. This gives us an indirect credence to rely on the first possibility. This suggests that the electron transfer from

S^{2-} ligand to W(VI) takes place to make it W(IV) via a kinetically competent W(V) species. The electron transfer pathway can be described as shown in Eqn. (4.11).
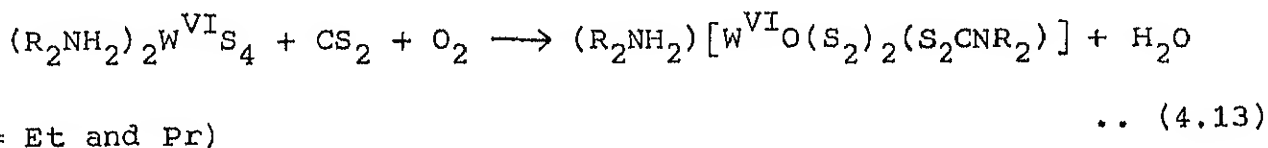
$$\left\{W^{VI}\overset{S}{\underset{S}{<}}\right\} \xrightarrow{O_2} \left\{W^V\overset{S}{\underset{S}{<}}\right\} + O_2^- \longrightarrow \left\{W^{IV}<\right\} + O_2 \longrightarrow \text{product} \quad\quad .. (4.11)$$
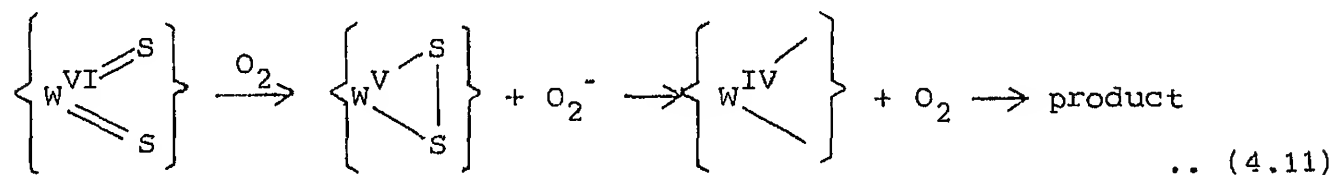
The above scheme where superoxide, O_2^- is generated, is verified by observing the conversion of benzyl bromide to benzyl alcohol.[135-138] Formation of benzyl alcohol was checked by adding benzyl bromide into the reaction mixture and stirring it for 20 hr. The benzyl alcohol thus formed was extracted with diethyl ether and identified by GC using the column AC-30. Thus, both internal and external oxidants share one electron each donated by two S^{2-} with the formation of one S_2^{2-}. The formation of W(IV) is then resulted by the reduction of W(V) by O_2^-. The last step i.e. the oxidation of W(IV) to the product is achieved by aerial oxygen. The entire process of this ligand to metal electron flow is controlled by external oxidant, oxygen, functioning as terminal electron acceptor. The role of tungsten is to function as an electron sink.

The product $[W^{VI}OS_2(S_2CNEt_2)_2]$ has also been achieved by reacting WOS_3^{2-} with tetraethyl thiuram disulfide at ambient temperature as shown below:

$$(NH_4)_2W^{VI}OS_3 + Et_2N-C\overset{S}{\underset{S-S}{<}}\overset{S}{\underset{}{>}}C-N Et_2 \longrightarrow [W^{VI}O(S_2)(S_2CNEt_2)_2]$$
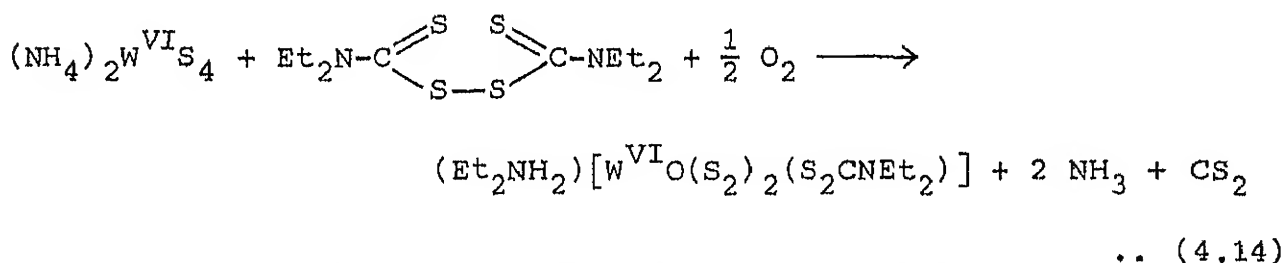
$$+ 2 NH_3 + H_2S \quad .. (4.12)$$

In this reaction there is no involvement of the metal center. The molybdenum analog of this compound is well known and has been synthesized by several different procedures.[42,63,94] But none of these methods work in case of tungsten.
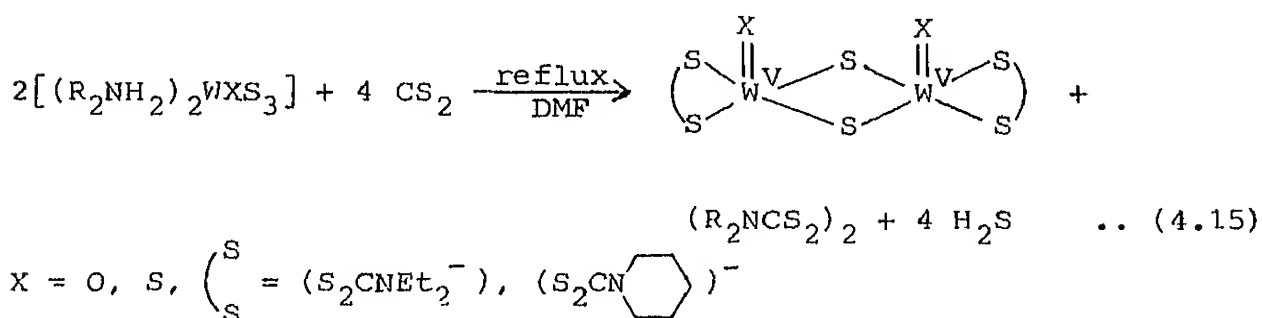
Similar reaction with less amount of CS_2 in the presence of oxygen leads to the conversion of $(R_2NH_2)_2WS_4$ to $(R_2NH_2)[W^{VI}O(S_2)_2-(S_2CNR_2)]$. Though CS_2 was added more than the stoichiometric ratio to convert both the secondary amines to $(S_2CNR_2)^-$, yet the conversion of only one mole of amine to $(S_2CNR_2)^-$ is surprising and in fact leads to the stepwise formation of $(S_2CNR_2)^-$ even in the preparation of $[W^{VI}O(S_2)(S_2CNR_2)_2]$ (Reaction 4.10) (vide supra). The reaction is analogous to earlier one and the involvement of intermediate ESR active W(V) along with the generation of O_2^- suggests a very similar induced electron transfer reaction concealed under purely ligand based reaction:

$$(R_2NH_2)_2W^{VI}S_4 + CS_2 + O_2 \longrightarrow (R_2NH_2)[W^{VI}O(S_2)_2(S_2CNR_2)] + H_2O$$

$$(R = Et \text{ and } Pr) \qquad \qquad \qquad .. \ (4.13)$$

The product $(Et_2NH_2)[W^{VI}O(S_2)_2(S_2CNEt_2)]$ has also been achieved by reacting WS_4^{2-} and tetraethylthiuram disulfide in the presence of oxygen at high temperature. This is a complicated ligand based redox reaction followed by decomposition of $S_2CNEt_2^-$.

$$(NH_4)_2W^{VI}S_4 + Et_2N-C{\overset{S}{\underset{S-S}{\diagup}}}{\overset{S}{\diagdown}}C-NEt_2 + \tfrac{1}{2} O_2 \longrightarrow$$

$$(Et_2NH_2)[W^{VI}O(S_2)_2(S_2CNEt_2)] + 2 \ NH_3 + CS_2$$

$$.. \ (4.14)$$

Tungsten(V)-sulfur complexes have generally been prepared by multi-step synthesis.[48,139,140] A new method for their efficient one-step synthesis has been developed. Gradual heating of diethylaminium and piperidinium thiotungstates (WOS_3^{2-}, WS_4^{2-}) with excess CS_2 in DMF affords desired compounds, with the overall reaction as shown in Eqn. (4.15):

$$2\left[(R_2NH_2)_2WXS_3\right] + 4\ CS_2 \xrightarrow[\text{DMF}]{\text{reflux}} \left(\begin{array}{c} X \\ \| \\ W^V \end{array} \cdots \right) +$$

$$(R_2NCS_2)_2 + 4\ H_2S \qquad .. \ (4.15)$$

$$X = O,\ S,\ \left(\begin{array}{c} S \\ \| \\ S \end{array} = (S_2CNEt_2^{-}),\ (S_2CN\bigcirc)^{-}\right.$$

The formation of H_2S and thiuram disulfide as byproducts of the reaction establishes the stoichiometry of the reaction. The formation of thiuram disulfide is confirmed by comparison with an authentic sample (tlc). In the synthesis of $W_2^VS_2(\mu-S)_2^{-}$ $(S_2CNR_2)_2$, compound $W_2^VOS(\mu-S)_2(S_2CNR_2)_2$ is formed as byproduct by the hydrolysis of $W_2S_2(\mu-S)_2(S_2CNR_2)_2$ with the traces of moisture present in the reaction medium. The characterization of thiuram disulfide as a byproduct shows that it is a thermally induced redox reaction. Same reactants on prolonged stirring in air produce $[WOS_2(S_2CNR_2)_2]$ in good yield involving induced internal electron transfer process using aerial oxygen as external oxidant (vide supra). This compound on heating in DMF gives the dinuclear compound in good yield. The nature of this reaction

(Eqn. 4.16) has been established as shown below:

$$2[W^{VI}O(S_2)(S_2CNEt_2)_2] \xrightarrow{DMF} [W_2^VO_2(\mu-S)_2(S_2CNEt_2)_2] + (Et_2NCS_2)_2$$
$$+ 2 S^0 \quad ..(4.16)$$
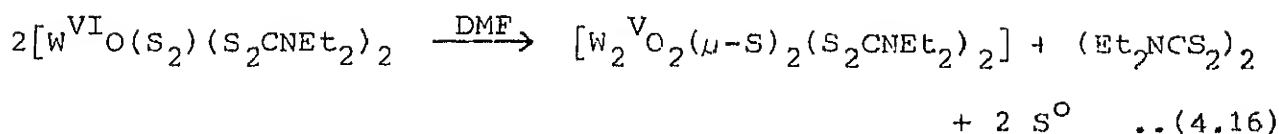
This reaction accounts for the reduction of two W(VI) of $[W^{VI}O(S_2)-(S_2CNEt_2)_2]$ to form W(V) dimer with the oxidation of two $(Et_2-NCS_2)^-$ to give one tetraethylthiuram disulfide. The formation of elemental sulfur could be accounted for through thermal cleavage of S_2^{2-} to S^{2-} and S^0. Thus the reaction (Eqn. 4.17) can best be described as thermally induced internal electron transfer reaction. Under vigorous reaction conditions and even by photochemical irradiation similar disproportionation reaction is envisaged.[31,32] Another example of this type of reaction where $(Et_2NH_2)[WO(S_2)_2-(S_2CNEt_2)]$ in solution (DMF or DMSO) at room temperature slowly changes to the dinuclear compound is shown in the following Equation (4.17):

$$2(Et_2NH_2)[WO(S_2)_2(S_2CNEt_2)] \xrightarrow{DMF} [W_2O_2(\mu-S)_2(S_2CNEt_2)_2]$$
$$+ 2 Et_2NH + H_2S + 5 S^0 \quad ..(4.17)$$
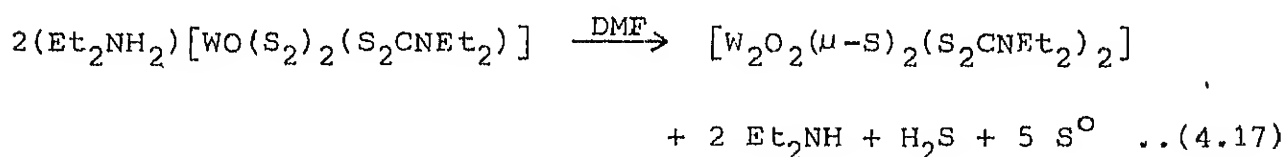
Here the coordinated S_2^{2-} ligands do not simply cleave to produce S^{2-} and S^0 but also induce the reduction of W(VI) to yield W(V) dimer. The overall reaction for S_2^{2-} ligand is a disproportionation reaction to supply the necessary electrons to reduce the metal centers further.

$$4 \ S_2{}^{2-} \ \longrightarrow \ 5 \ S^0 + 3 \ S^{2-} + 2 \ e^- \qquad\qquad .. \ (4.18)$$
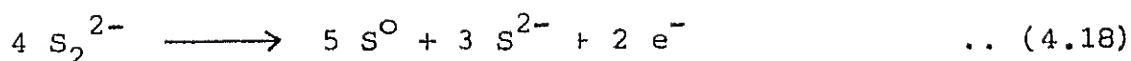
The reaction of $(NH_4)_2WS_4$ & $(Et_2NCS_2)_2$ gives $[W_2S_2(\mu-S)_2(S_2CNEt_2)_2]$ in low yield. The low yield may be due to the formation of $(NH_4)_2S_x$ as a byproduct which combines with sulfur to give poly-sulfide. Polysulfide acts as an external reductant and oxidizes the product back to W(VI). However, the yield of product can be improved if a strong jet of argon is used over the surface of the reaction mixture to flush and the $S_x{}^{2-}$ formed. The $S_2{}^{2-}$ ligand in $[W^{VI}O(S_2)(S_2CNR_2)_2]$, reacts readily with nucleophiles resulting in a sulfur transfer reaction, producing sulfur substituted nucleophile and a product $[W^{IV}O(S_2CNR_2)_2]$ with reduced metal center. The nucleophiles react with persulfido ligand of the complex in a straightforward pathway· the S-S and W-S bonds are cleaved and sulfur atom transfer to the nucleophile is effected (Eqn. 4.19):

$$[W^{VI}O(S_2)(S_2CNR_2)_2] + 2 \ \text{nucleophile} \longrightarrow [W^{IV}O(S_2CNR_2)_2]$$
$$+ \ 2 \ S = \text{nucleophile} \qquad .. \ (4.19)$$
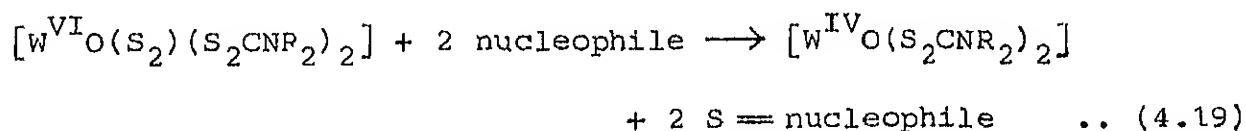
The substituted nucleophiles have been identified by IR and chemical analysis.

Another interesting reaction is the regeneration of W(VI) complex. When the complex $[W^{IV}O(S_2CNR_2)_2]$ is treated with elemental sulfur, the coordinatively unsaturated W(IV) species undergoes the expected oxidative addition reaction. Conversion of 2 S^0 to $S_2{}^{2-}$ and W(IV) to W(VI) furnishes the electron balanced

reaction. Similar observations in analogous molybdenum systems, have also been reported.[63,141] The only difference lies in the fact that the tungsten analogs are more stable.

4.2   Structural Aspects of the Synthesized Complexes

4.2.1   Infrared Spectra

Infrared spectroscopy can reasonably determine the structural aspects   of the synthesized complexes. For S_2^{2-} coordinated complexes, the identification of ν (S-S) mode of vibration is relatively an easy task. This is because of the fact that the ν(S-S) mode of vibration for S_2^{2-} is a strong one and normally appears in the region 480 - 600 cm^{-1}.[69] However, the situation becomes complicated when in addition to S_2^{2-} chelating ligand, the compound contains a terminal sulfido group, ν(W-S$_t$),which appears in the range 490 to 550 cm^{-1} (vide infra, Table 1.1). Thus, the identification of both the functional groups present together in the same compound may raise problems. The exact position of ν(W-S$_t$) mode of vibration is dependent upon the oxidation state of tungsten and the geometry of the complex. Distinction between these two modes of vibrations can be made readily if the oxo analog of the sulfido complex can be synthesized. In the case of oxo analog of this compound, the region 480-600 cm^{-1} should show the presence of only ν(S-S) vibration. A comparison of this mode of vibration with that of the corresponding sulfur analog of the compound can thus help to resolve

the two vibrations related to $\nu(S-S)$ and $\nu(W-S_t)$ in this type of complexes.

The infrared spectra of the synthesized complexes containing these ligands are reproduced in Figs. 4.1.10 to 4.1.17. The comparison can be best represented by taking $[WO(S_2)(S_2CNEt_2)_2]$ and $[WS(S_2)(S_2CNEt_2)_2]$. In the former case a very strong absorption at 940 cm^{-1} can be readily assigned to $\nu(W=O)$ by comparing its spectrum with that of the reported molybdenum analog, $[MoO(S_2)-(S_2CNEt_2)_2]$.[94,141] The complex, $[MoO(S_2)(S_2CNEt_2)_2]$ shows $\nu(Mo=O)$ around 915 cm^{-1} which on resolution shows splitting at 908 cm^{-1} and 920 cm^{-1}. However, the corresponding complexes with other dithiocarbamates show only one strong absorption responsible for $\nu(Mo=O)$ in this region.[141] Recently, it has been observed that the solution spectrum of $[MoO(S_2)(S_2CNEt_2)_2]$ shows a single absorption at 920 cm^{-1} assignable to $\nu(Mo=O)$.[142] Splitting of this band is then probably due to solid state effect. In the tungsten complexes $\nu(W=O)$ appears around 940 cm^{-1} which is slightly higher than $\nu(Mo=O)$ observed in the corresponding molybdenum analogs. This suggests the involvement of stronger multiple bonding between tungsten and oxygen compared to molybdenum and oxygen. In all these tungsten complexes a band around 550 cm^{-1} of medium to strong intensity is assignable to $\nu(S-S)$ by comparing these with the corresponding molybdenum systems. It is to be noted that $\nu(S-S)$ vibration remains almost unaffected in the hepta-coordinated complexes of W(VI) and Mo(VI). On the

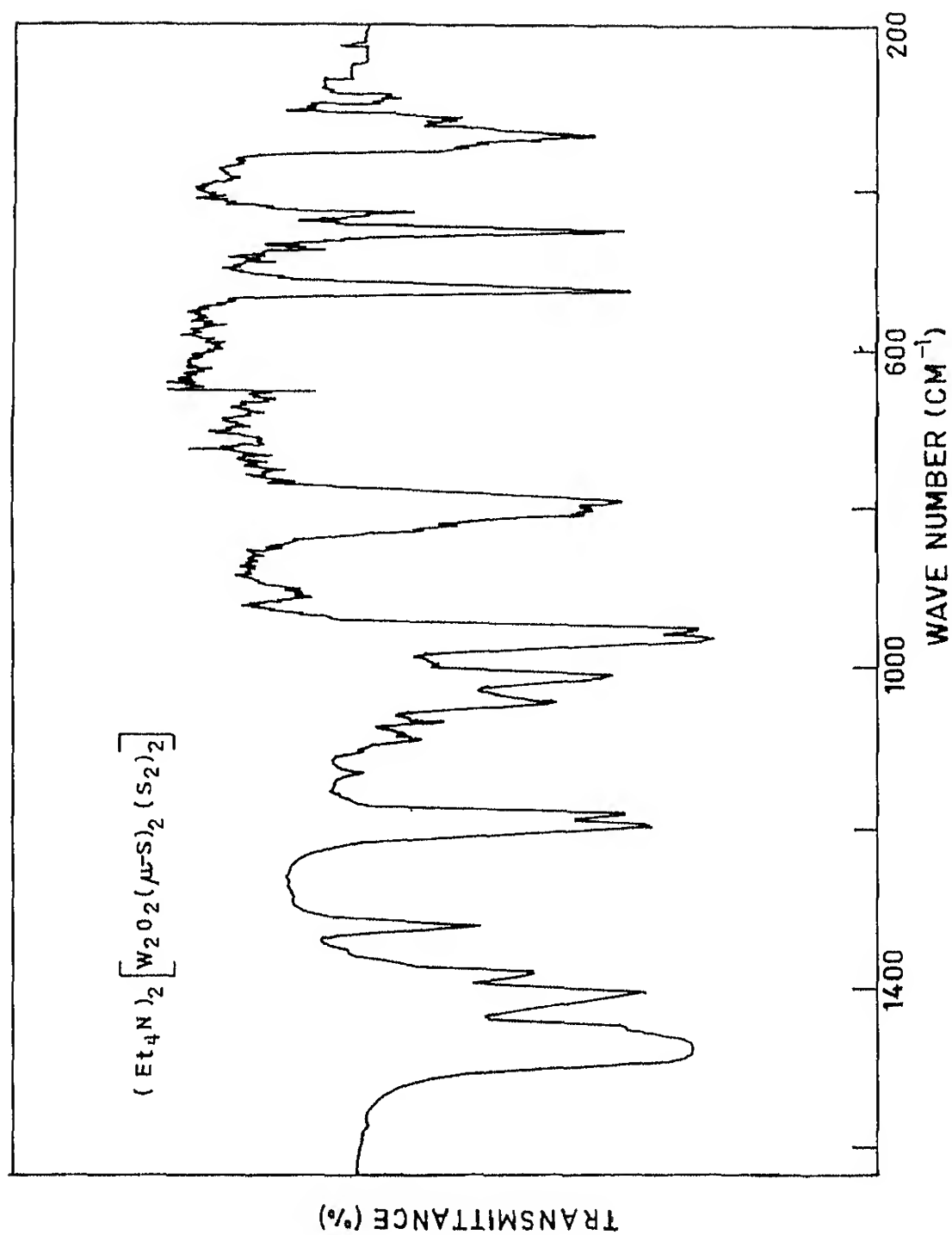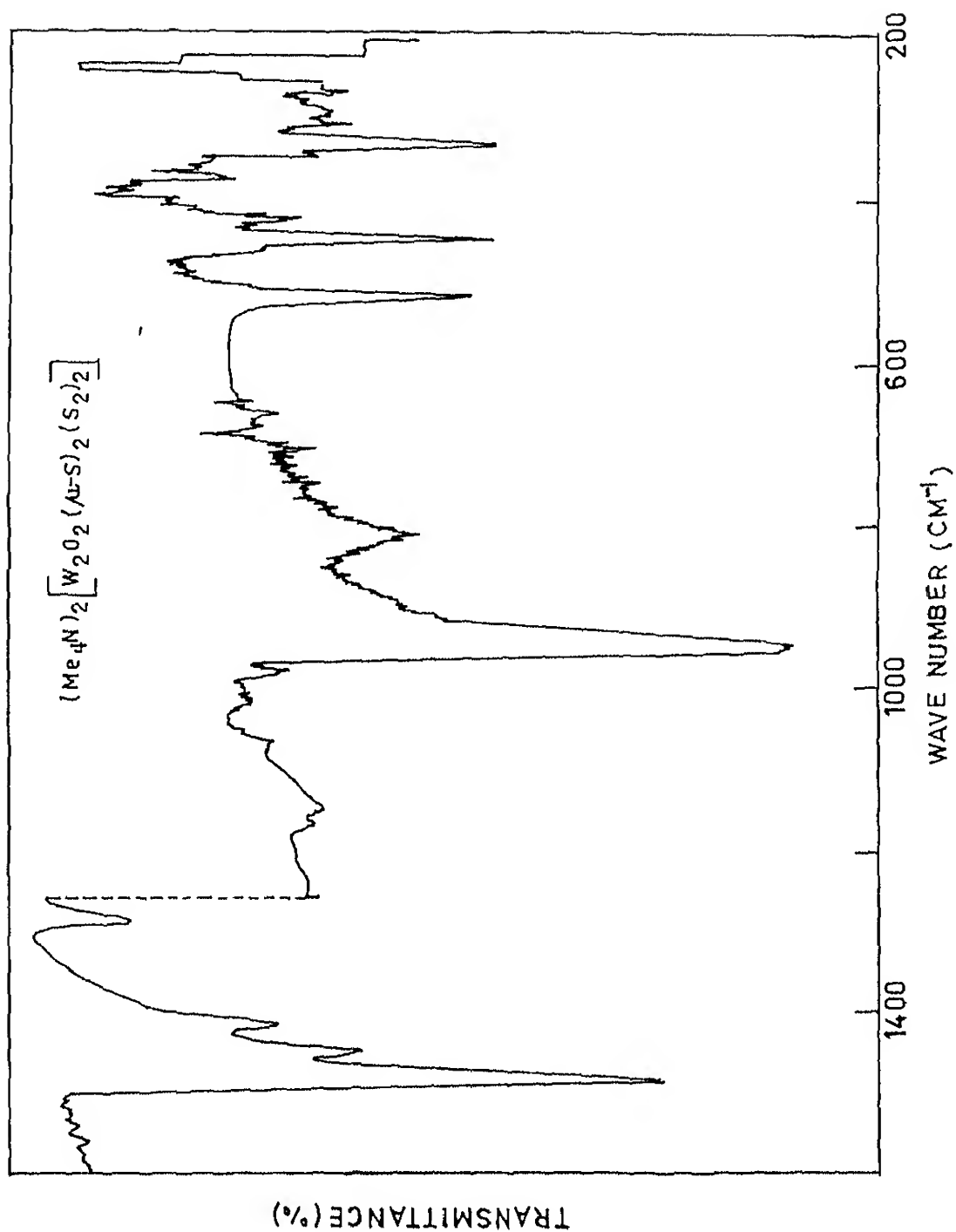$(Et_4N)_2 \left[W_2O_2(\mu-S)_2 (S_2)_2 \right]$

TRANSMITTANCE (%)

WAVE NUMBER (CM^{-1})

FIG. 4.1.1 INFRARED SPECTRUM

$(Me_4N)_2 \left[W_2 O_2 (\mu\text{-}S)_2 (S_2)_2 \right]$

TRANSMITTANCE (%)

WAVE NUMBER (CM^{-1})

FIG 4.1.2 INFRARED SPECTRUM

$(Et_4N)_2[W_3S_9]$

FIG. 4.1.3 INFRARED SPECTRUM

WAVE NUMBER (CM^{-1})

TRANSMITTANCE (%)

76

$(Ph_4As)_2[W_3S_9]$

TRANSMITTANCE (%)

WAVE NUMBER (CM^{-1})
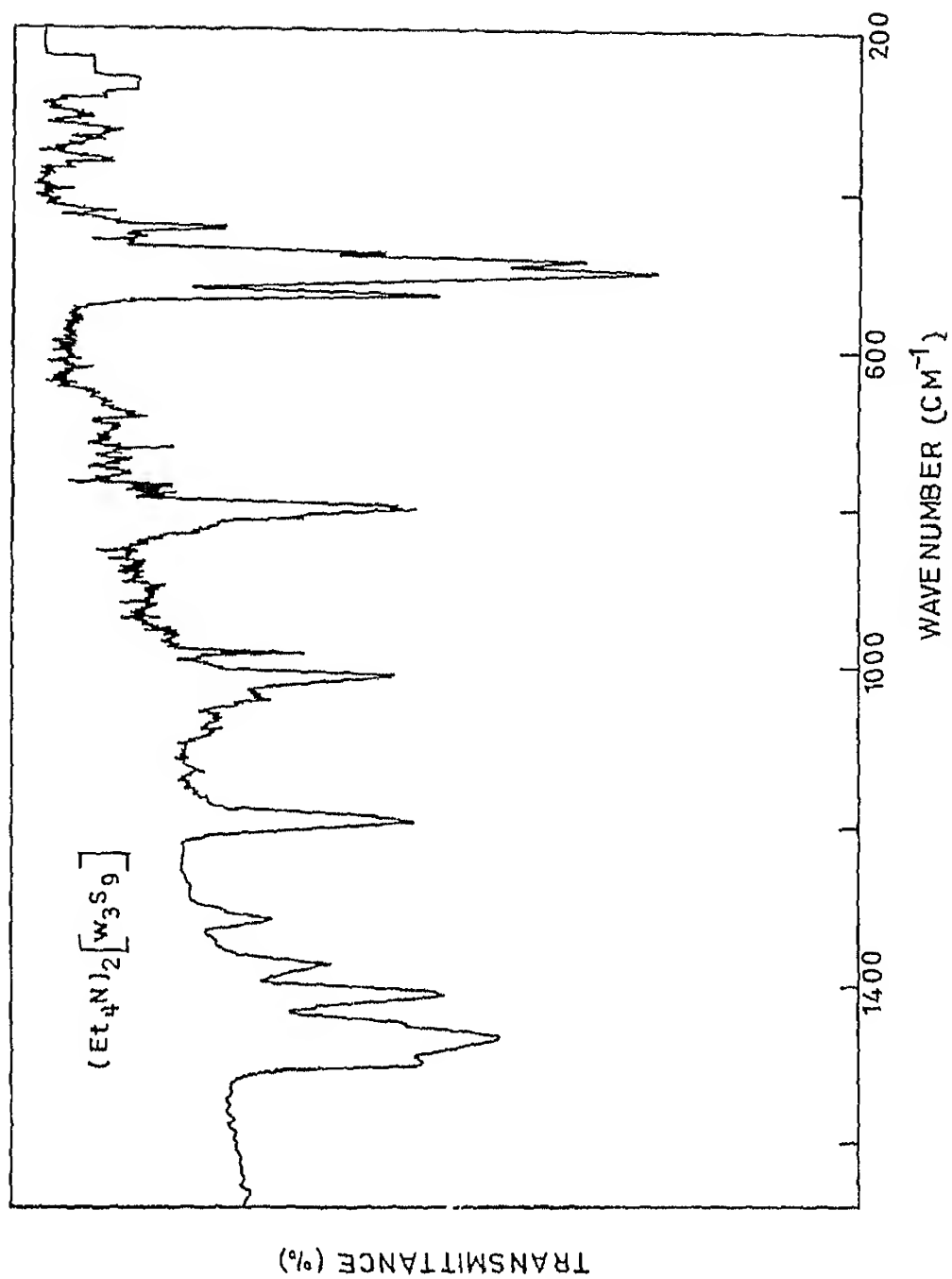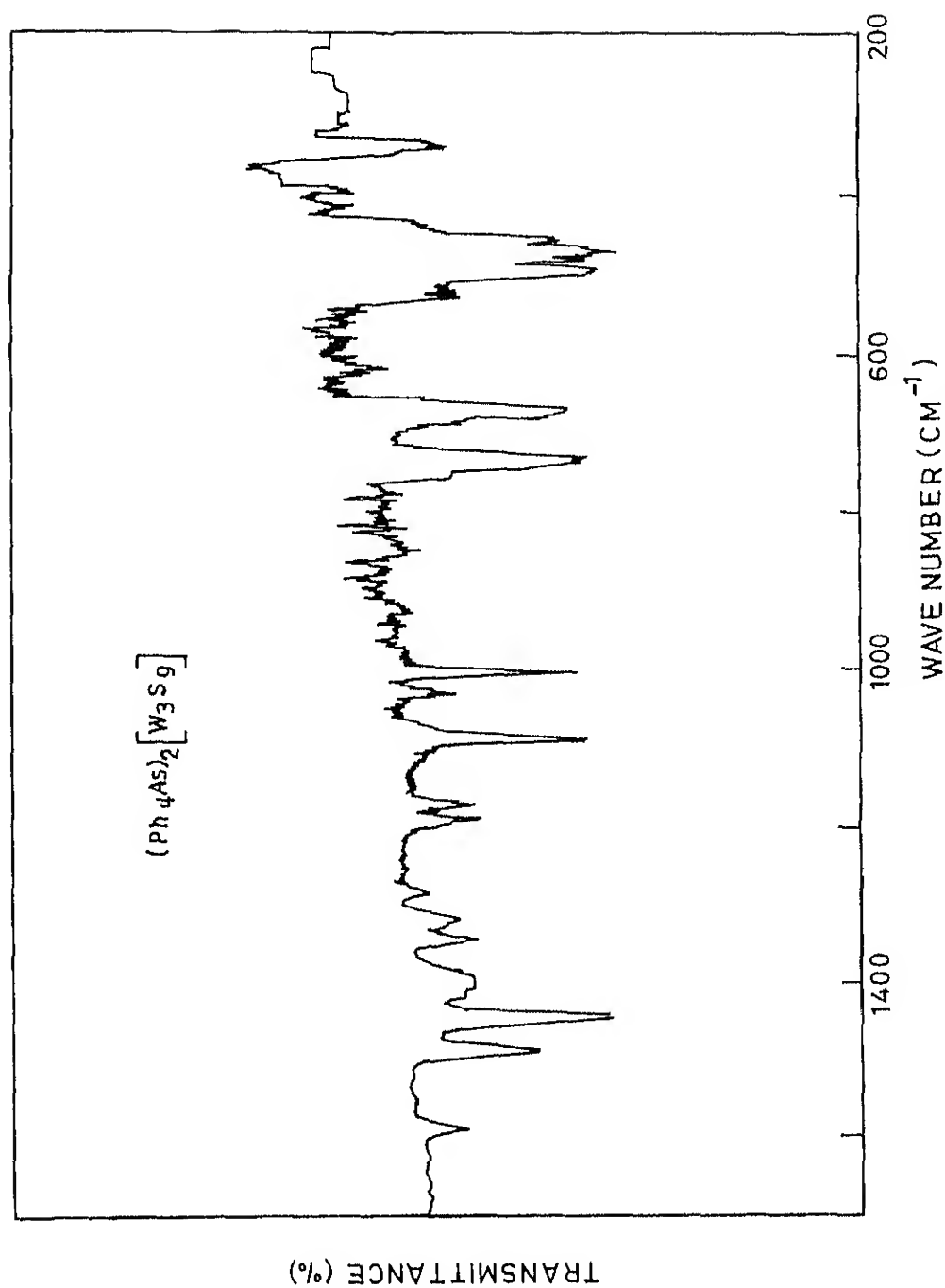
FIG 4.1.4 INFRARED SPECTRUM

FIG. 4.1.5 INFRARED SPECTRA
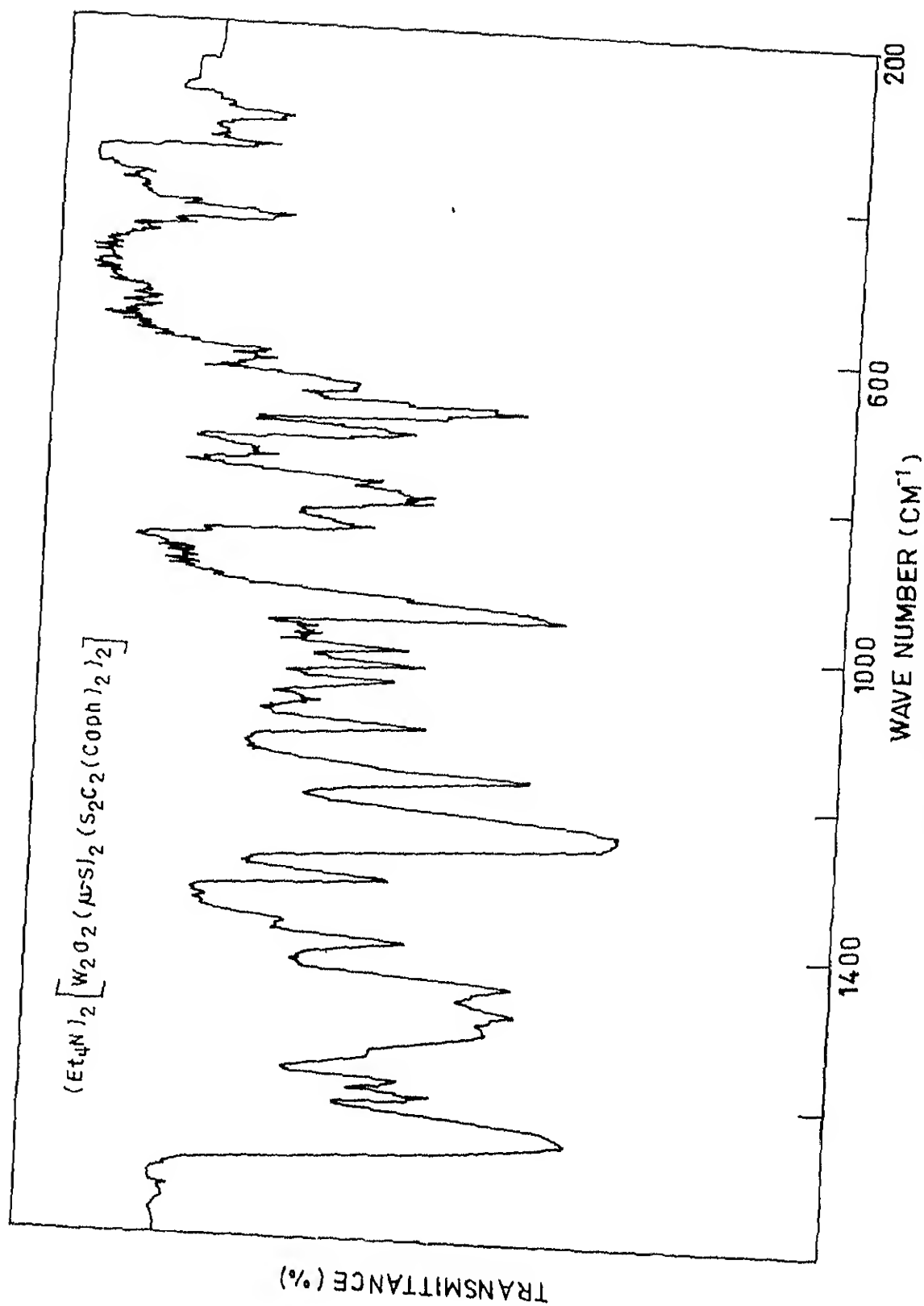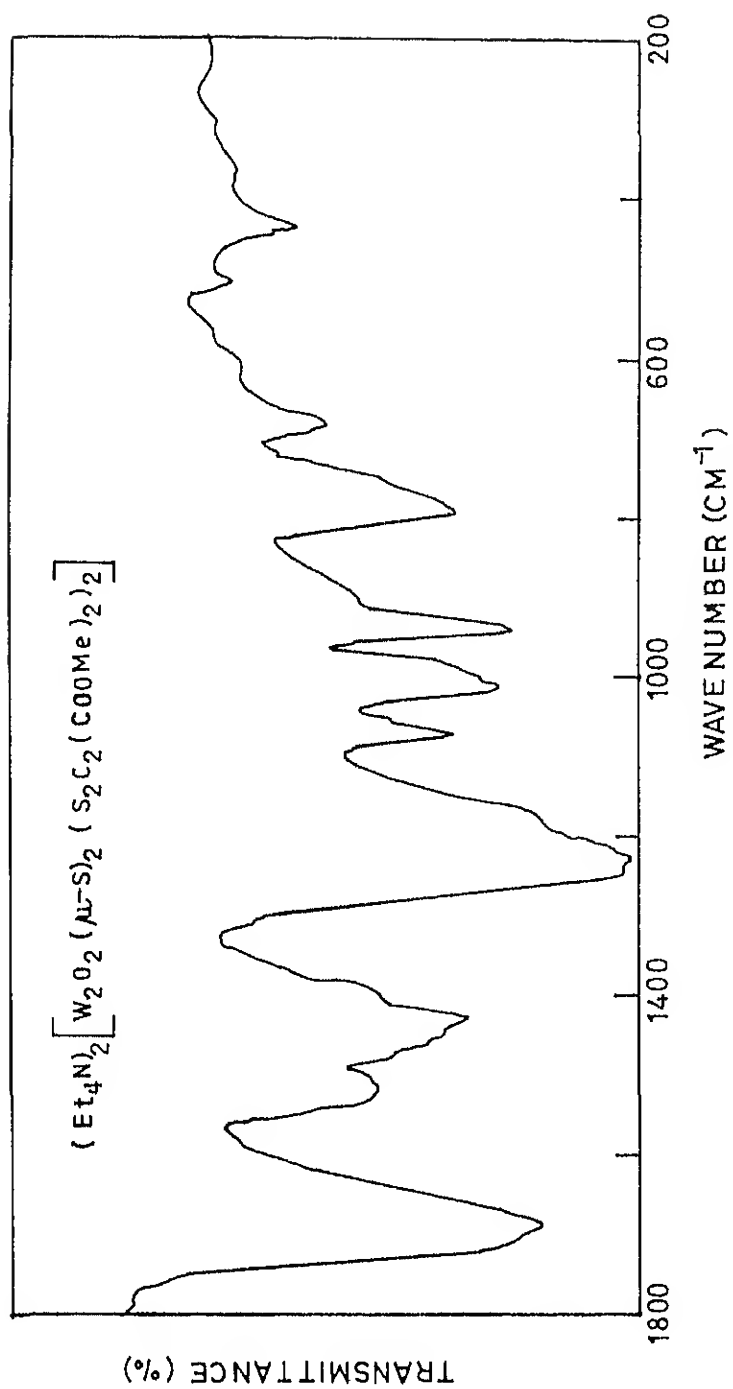
$(Et_4N)_2 \left[W_2O_2(\mu\text{-}S)_2 (S_2C_2(COph)_2)_2 \right]$

TRANSMITTANCE (%)

WAVE NUMBER (CM^{-1})

FIG. 4.1.6 INFRARED SPECTRUM

$(Et_4N)_2 \left[W_2O_2(\mu-S)_2(S_2C_2(COOMe)_2)_2 \right]_2$

FIG 417 INFRARED SPECTRUM

WAVE NUMBER (CM^{-1})

TRANSMITTANCE (%)

FIG. 4.1.8   INFRARED SPECTRA

$K_4\left[W_2O_2(\mu=S)_2(CN)_6\right].3H_2O$

WAVE NUMBER (CM^{-1})

FIG 4 1.9 INFRARED SPECTRUM

TRANSMITTANCE (%)

$$\left[WO(S_2)(S_2CNEt_2)_2 \right]$$

TRANSMITTANCE (%)

WAVE NUMBER (CM^{-1})
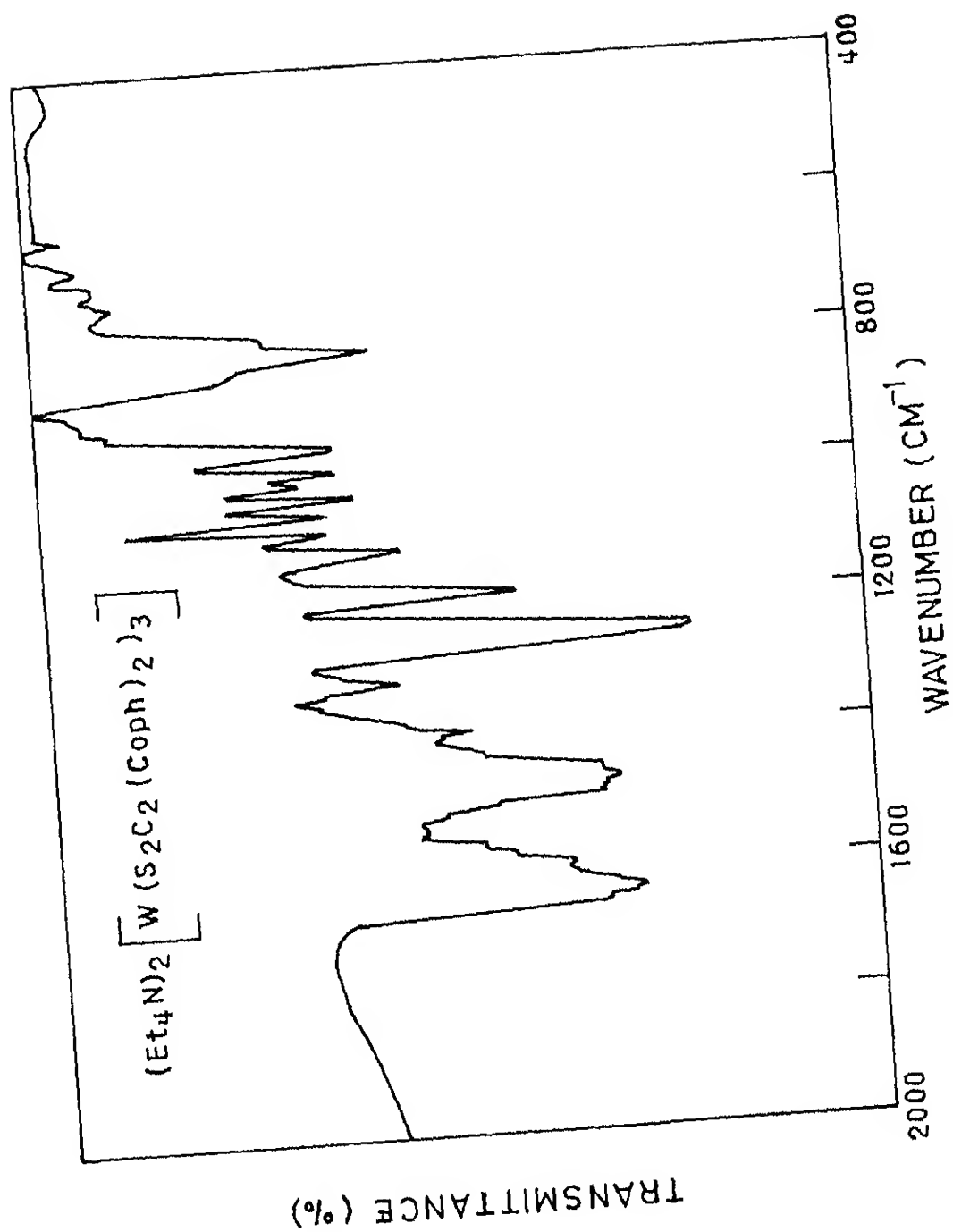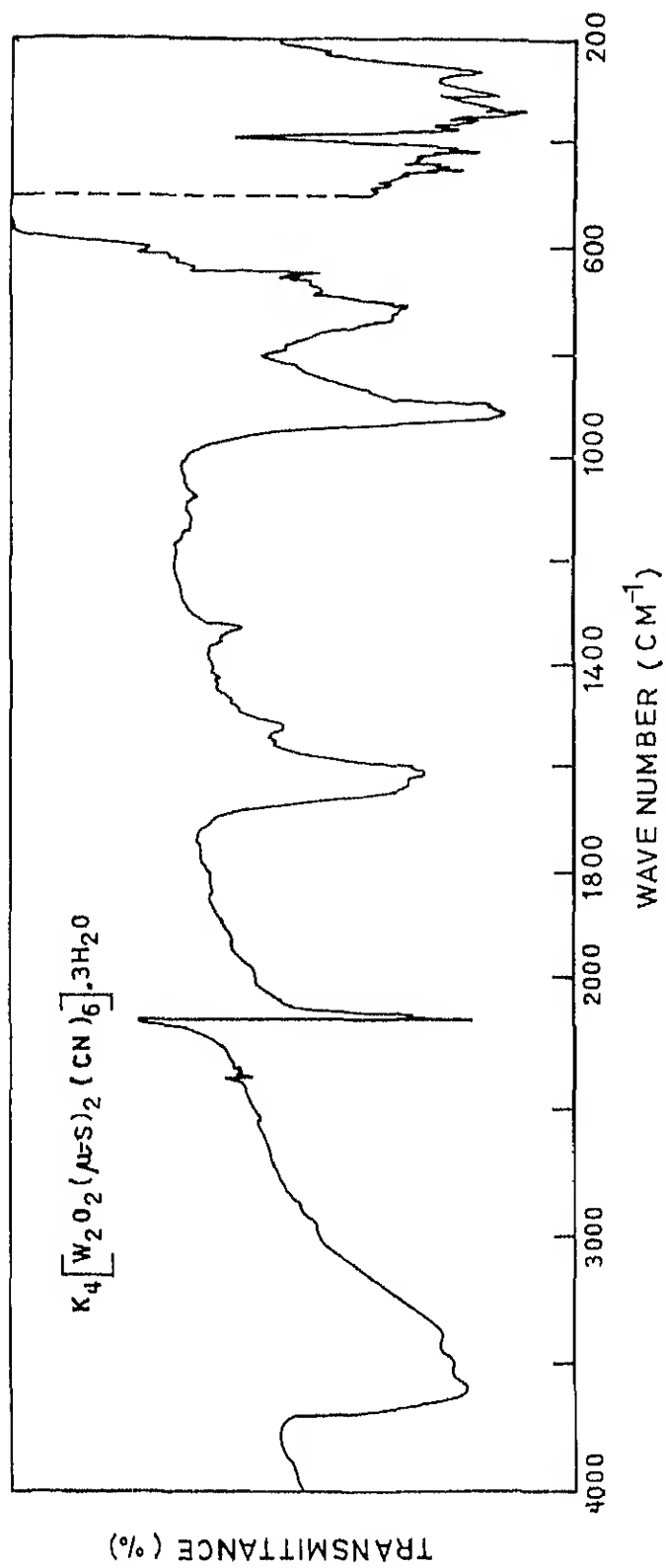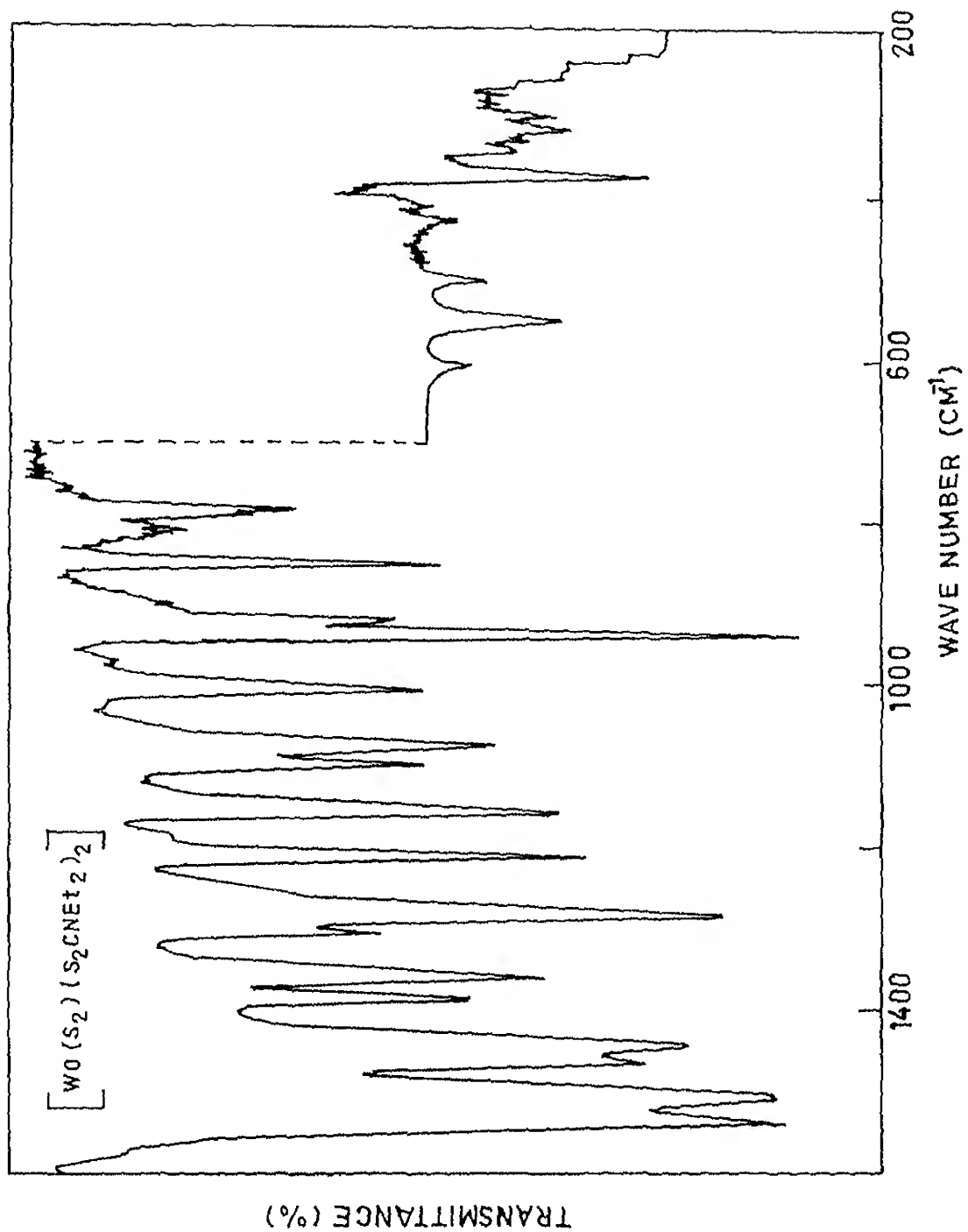
FIG. 4.110 INFRARED SPECTRUM
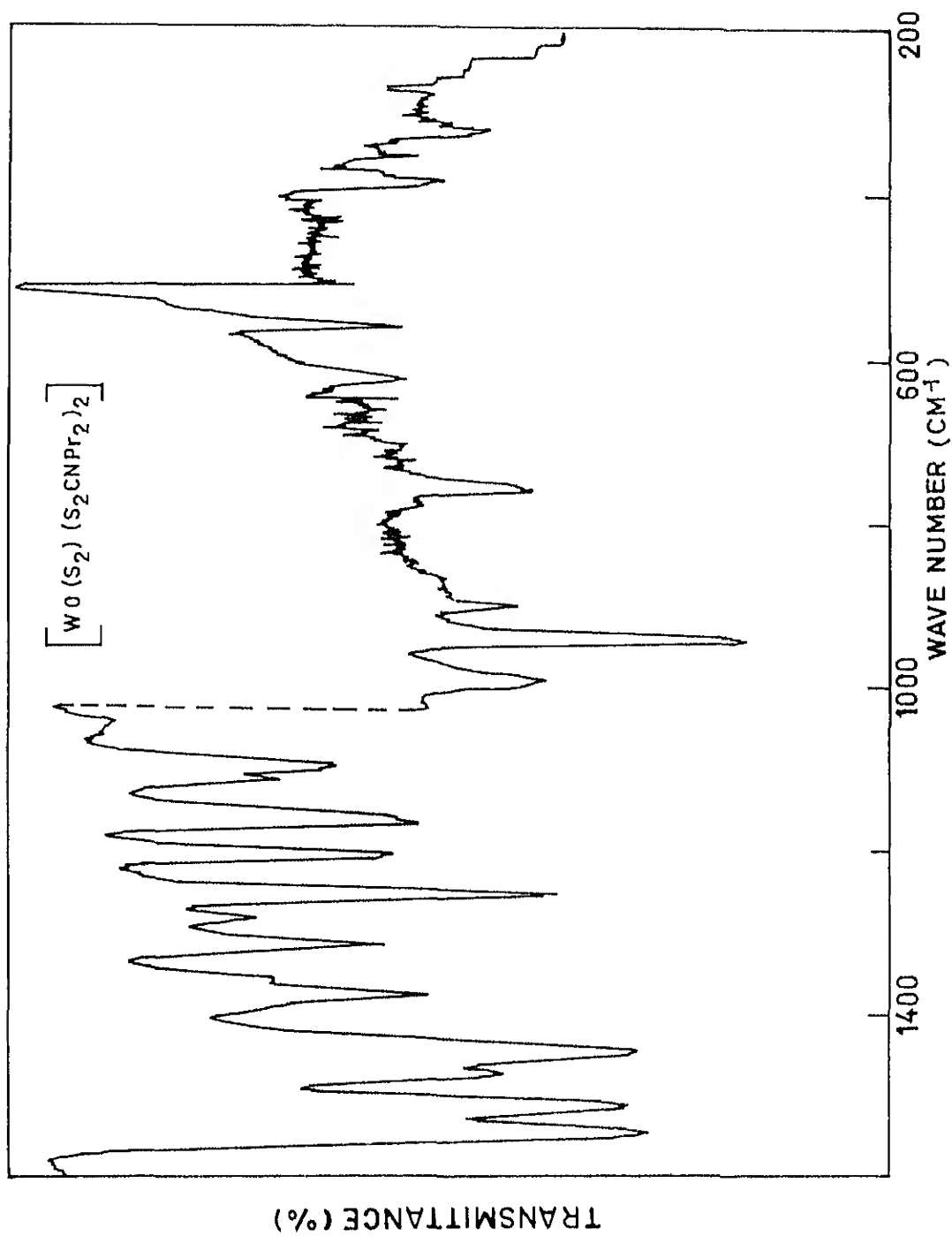
83

FIG. 4.1.11 INFRARED SPECTRUM

WAVE NUMBER (CM^{-1})

TRANSMITTANCE (%)

$\left[WO(S_2)(S_2CNPr_2)_2 \right]$

FIG 4.1.12   INFRARED SPECTRUM

$$[WS (S_2) (S_2 CNEt_2)_2]$$

TRANSMITTANCE (%)

WAVE NUMBER (CM^{-1})

FIG. 4 1.13   INFRARED SPECTRUM

$\left[WS(S_2)(S_2CNPr_2)_2 \right]$

TRANSMITTANCE (%)

WAVE NUMBER (CM^{-1})
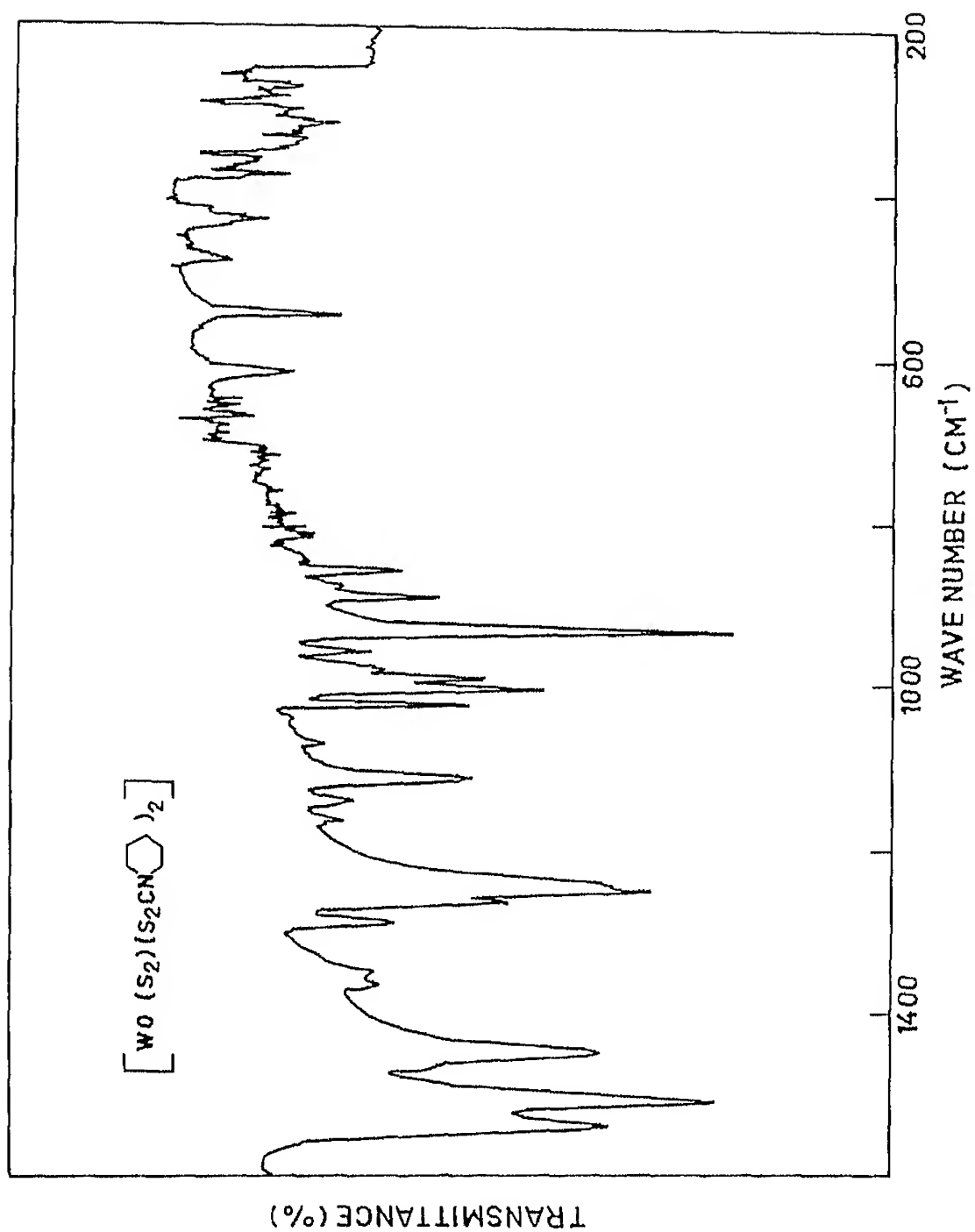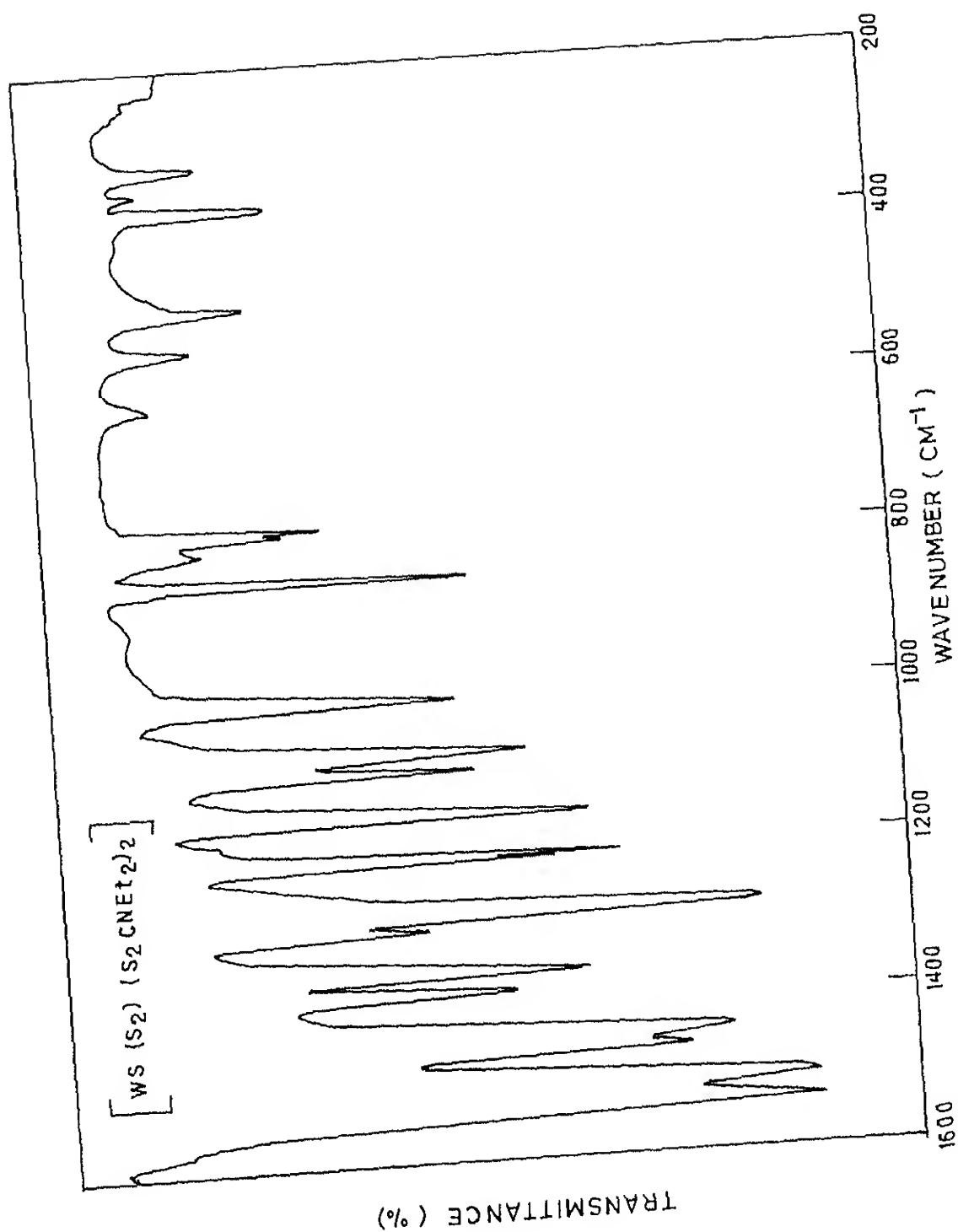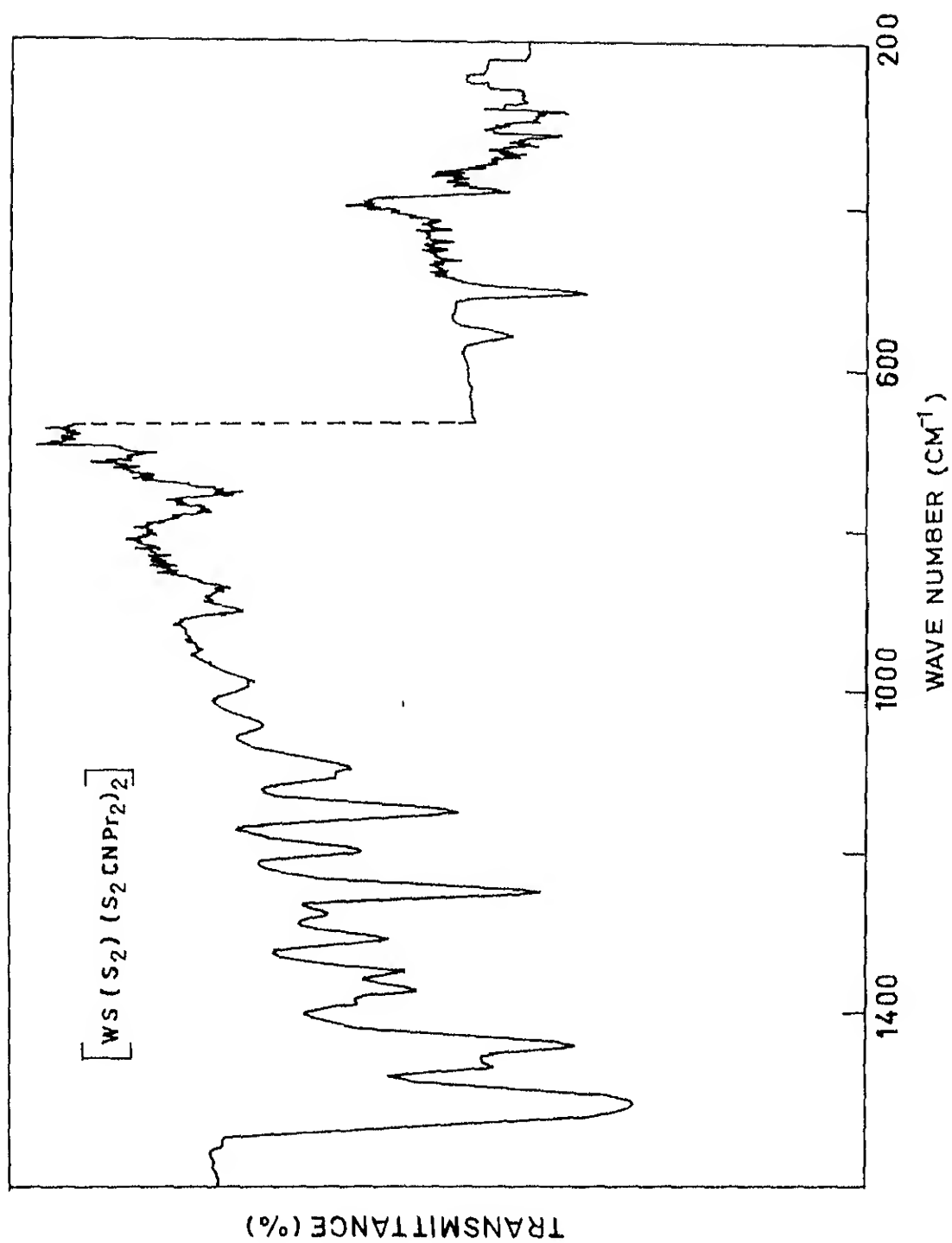
FIG. 4.114 INFRARED SPECTRUM
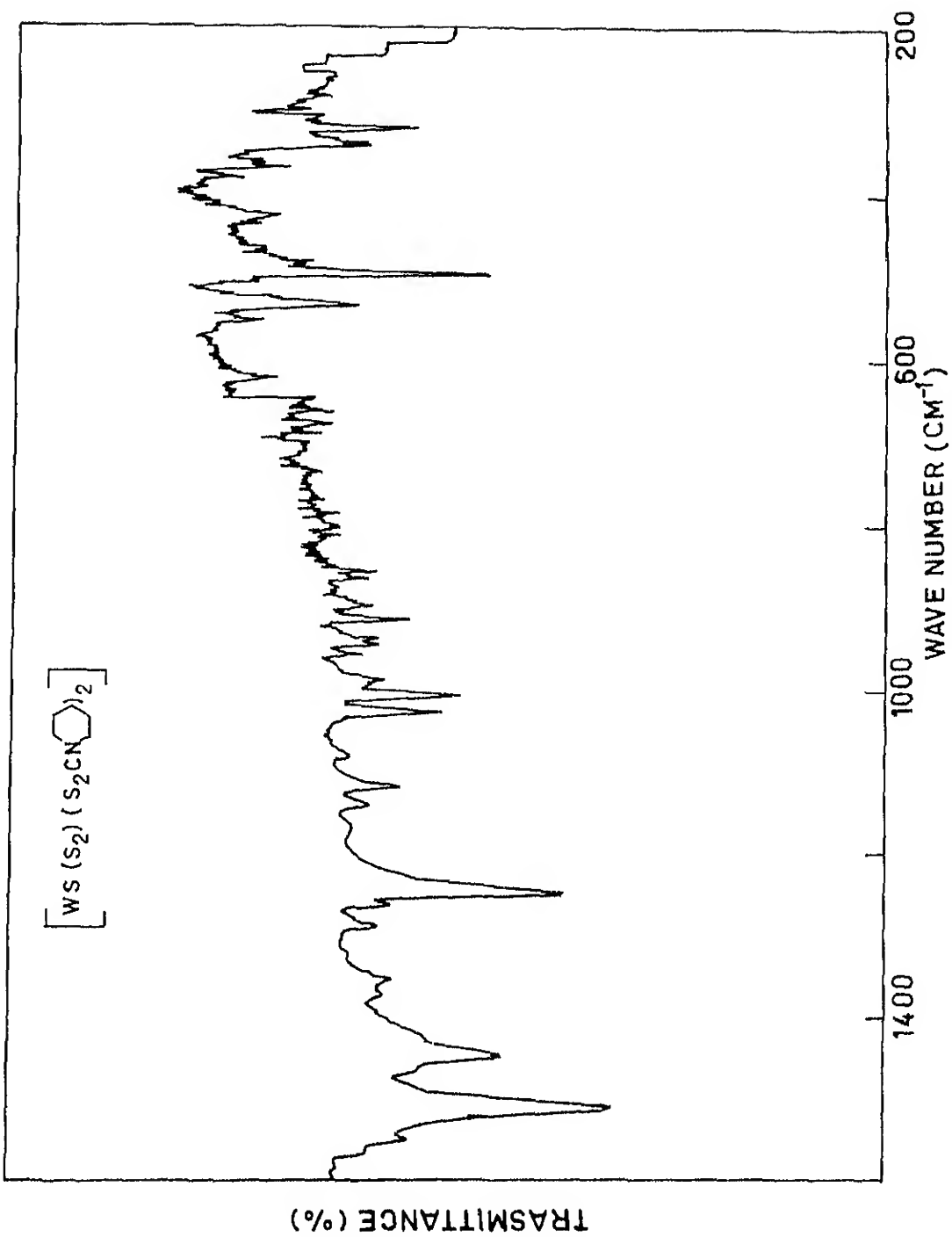
FIG. 4.1.15 INFRARED SPECTRUM

$$\left[WS\,(S_2)\,(S_2CN\bigcirc)_2 \right]$$

WAVE NUMBER (CM^{-1})

TRASMITTANCE (%)

$(Et_2NH_2) \left[WO(S_2)_2(S_2CNEt_2) \right]$

WAVE NUMBER (CM^{-1})

FIG. 4116 INFRARED SPECTRUM

TRANSMITTANCE (%)

$(Pr_2NH_2)\left[WO(S_2)_2(S_2CNPr_2)\right]$

WAVE NUMBER (CM^{-1})
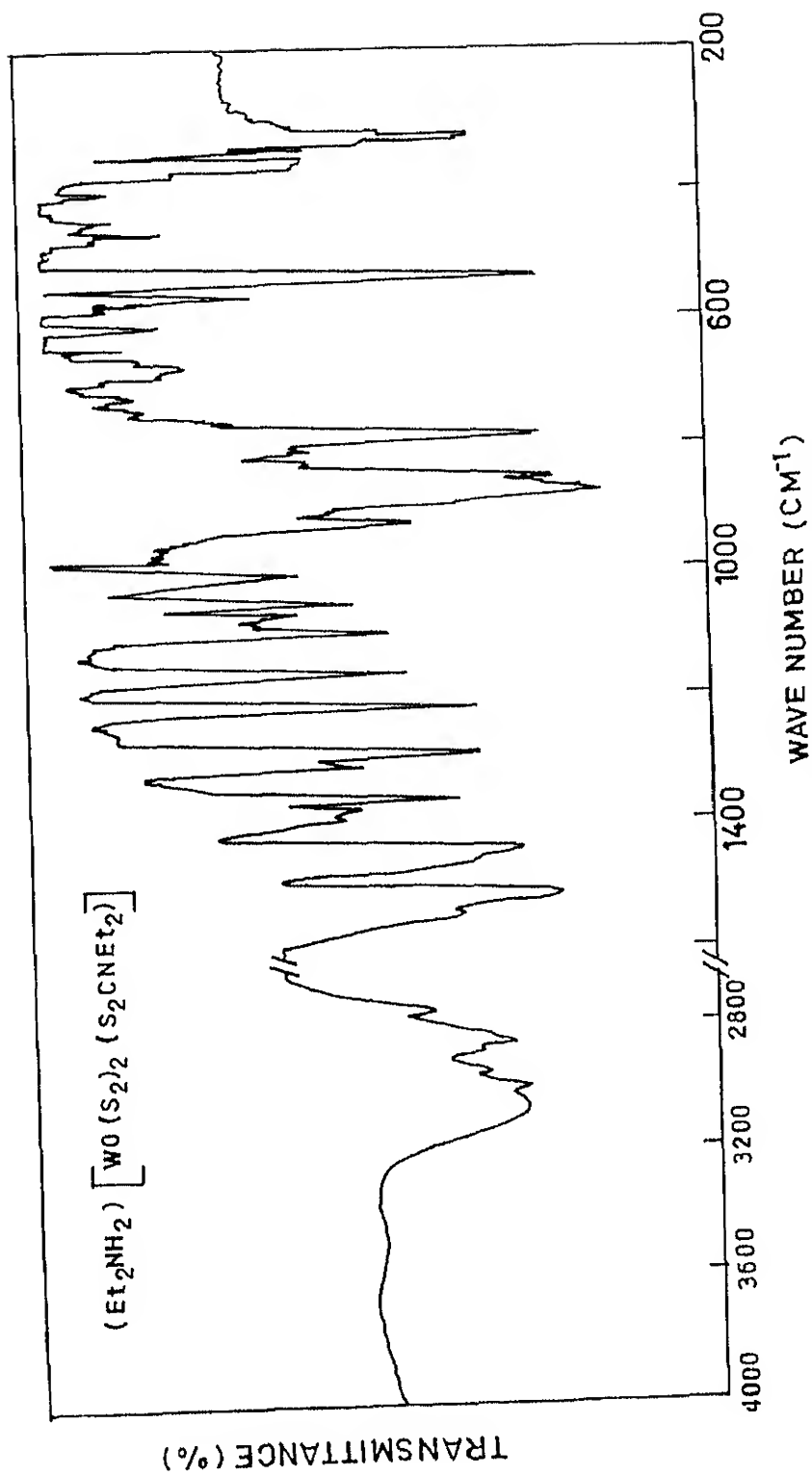
FIG. 4117 INFRARED SPECTRUM

TRANSMITTANCE (%)
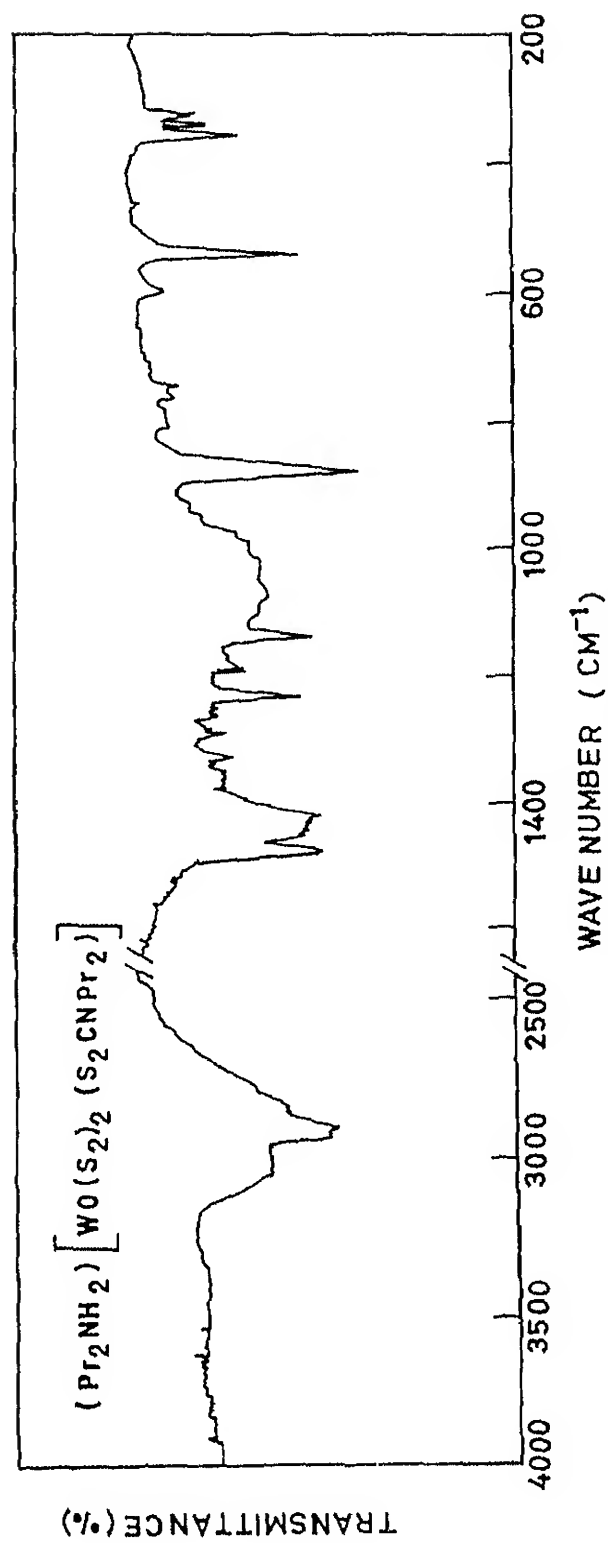
basis of these observations one can now assign $\nu(W-S_t)$ in the
series of all sulfur compound like $[WS(S_2)(S_2CNEt_2)_2]$. The IR
spectra of this class of compounds are reported in Figs. 4.1.13
to 4.1.15. The band appearing at 500 cm^{-1} is then assigned to
$\nu(W-S_t)$ and the appearance of another band in the range of 535 to
550 cm^{-1} is then responsible for $\nu(S-S)$ vibration. This assign-
ment is in good agreement with the data reported by Stiefel and
coworkers[42] for the corresponding $(S_2CNBu_2)^-$ ligated compound.
Identification of $\nu(W-S_2)$ is a difficult task because of the
presence of thiocarbamate in the compound. When S_2^{2-} is coordi-
nating in a side on fashion, the local symmetry of $\{W {\overset{S}{\underset{S}{<}}} |\}$ is
C_{2v}, for which the expected normal mode of vibrations, are $\nu(S-S)$
(A_1), ν_s, $\nu(W-S)$, (A_1) of $\{W {\overset{S}{\underset{S}{<}}} |\}$ moiety and ν_{as}, $\nu(W-S)$, (B_1) of
$\{W {\overset{}{\underset{S}{<}}} |\}$ moiety, respectively. All these vibrations are IR active.
The exact identification of the ν_s and ν_{as} vibrations would be
difficult because of the presence of other vibrations arising
from dithiocarbamate coordinated to tungsten as well as the possi-
bility of strong coupling of A_1 mode of vibration with that of
$\nu(S-S)$. The vibrations due to the presence of other ligand can
be to some extent identified by comparing the infrared spectrum
of $[WO(S_2CNR_2)_2]$ (Fig. 4.1.18) with the hepta-coordinated systems.
Fig. 4.1.18 shows several absorptions in the far infrared region
mainly originating from $(S_2CNR_2)^-$ vibrations. Though the geometry,
coordination number and oxidation state of this complex differ
with the hepta-coordinated complexes yet a tentative comparison
can be made. Once ν_s $\{W {\overset{S}{\underset{S}{<}}} |\}$ and ν_{as} $\{W {\overset{S}{\underset{S}{<}}} |\}$ are roughly located,

$[WO(S_2CNEt_2)_2]$

TRANSMITTANCE (%)

WAVE NUMBER (CM^{-1})
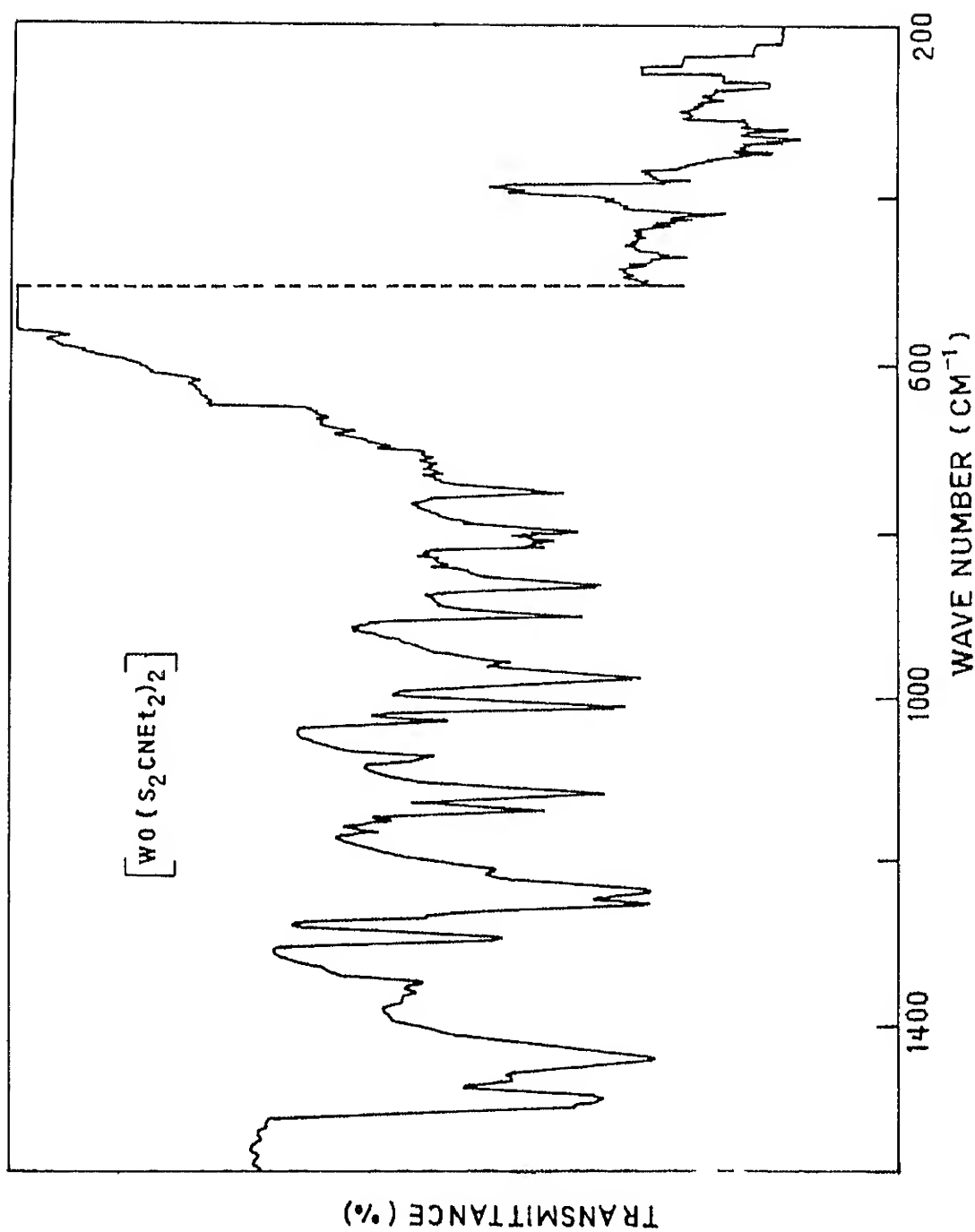
FIG. 4.1.18 INFRARED SPECTRUM
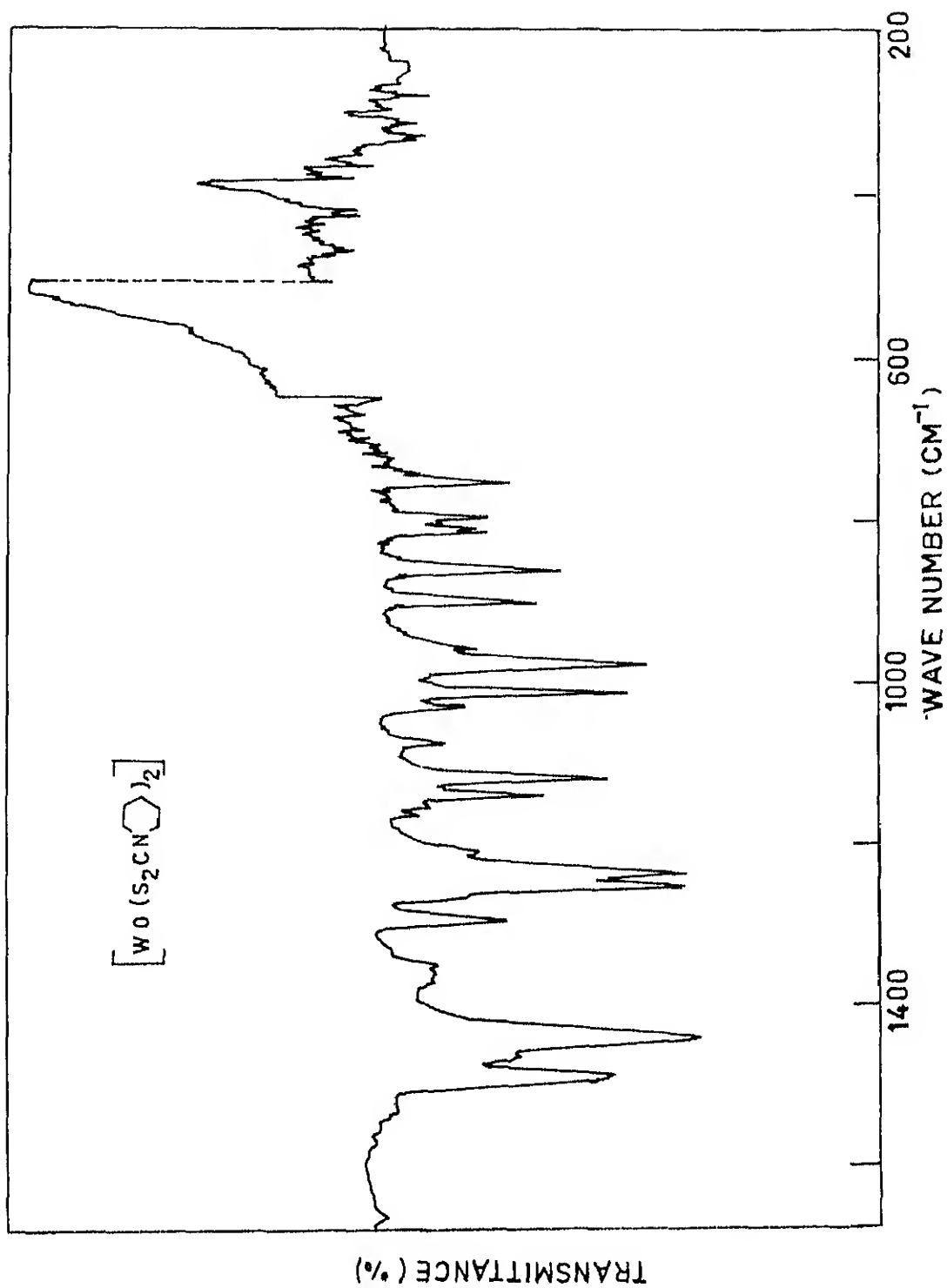
FIG 4.1.19 INFRARED SPECTRUM

$\left[W O (S_2 CN \bigcirc)_2 \right]$

-WAVE NUMBER (CM^{-1})

TRANSMITTANCE (%)

a comparison with another class of compound, $[W_2O_2(\mu\text{-S})_2(S_2)_2]^{2-}$ which does not have dithiocarbamate ligand, can be made. Proceeding in this direction, we identified these vibrations appearing around 370 and 350 cm^{-1} for $\nu_s\{W{<}{\overset{S}{\underset{S}{|}}}\}$ and $\nu_{as}\{W{<}{\overset{S}{\underset{S}{|}}}\}$, respectively.

In the dimeric or trimeric compounds, additional vibrations due to $\nu(W\text{-}S_b)$ should appear along with the other functionalities present. The molybdenum-sulfur-molybdenum bridging vibrations are well documented by isotopic studies.[86] For the dimeric dithiocarbamate complexes of molybdenum(V) these vibrations are reported in the literature.[97] Comparing the tungsten(V) dithiocarbamato compounds, synthesized in the present investigation, with the corresponding molybdenum analogs the $\nu(W\text{-}S_b)$ vibrations can be reasonably assigned. Thus, comparing the spectra of these tungsten complexes with the reported molybdenum analogs, assignment for these vibrations are made which are presented in Tables 4.1, 4.2 and 4.4.

An important point worth mentioning regarding $\nu(W{=}O)$ vibrations of the tungsten compounds, is that it appears at a higher wave number compared to $\nu(Mo{=}O)$ vibration of the corresponding molybdenum compound. Though tungsten is heavier than molybdenum yet the appearance of this vibration at higher wave number is suggestive of greater multiple bonding between tungsten and oxygen compared to molybdenum and oxygen. For the molybdenum complex $(Et_4N)_2[Mo_2O_2(\mu\text{-}S_2)_2(S_2)_2]$ recent M.O. calculations suggest that the bond order of {Mo-O} moiety in the compound as high as 3.[29]

Table 4.1. Infrared Spectral Data

Complex	ν(Mo=O) (cm^{-1})	ν(S-S) (cm^{-1})	ν(M-S$_b$) (cm^{-1})	Other important frequency (cm^{-1})	Reference
(Me$_4$N)$_2$[Mo$_2$O$_2$(μ-S)$_2$(S$_2$)$_2$]	925(s)	516(m)	467(m)	357(w), 321(w) (ν Mo-S$_2$)	72
(Me$_4$N)$_2$[W$_2$O$_2$(μ-S)$_2$(S$_2$)$_2$]	950(s) 940(sh)	520(m)	450(m)	335(w) (νW-S$_2$)	This work
(Et$_4$N)$_2$[W$_2$O$_2$(μ-S)$_2$(S$_2$)$_2$]	960(s) 950(sh)	520	450(m)	335(w) (νW-S$_2$)	This work
(Et$_4$N)$_2$[W$_2$O$_2$(μ-S)$_2$(S$_2$C$_2$(COPh)$_2$)$_2$]	960(s) 955(sh)	-	440(m)	1660(s) (νC=O), 1453 (νC=C)	This work
(Et$_4$N)$_2$[W$_2$O$_2$(μ-S)$_2$(S$_2$C$_2$(COOMe)$_2$)$_2$]	950(s) 935(sh)	-	450(m)	1680(s) (νC=O), 1425(s) (νC=C)	This work
(Et$_4$N)$_2$[Mo$_2$O$_2$(u-S)$_2$(S$_2$C$_2$(COOMe)$_2$)$_2$]	947(s)	-	473(m)	-	68
(Et$_4$N)$_2$[W(S$_2$C$_2$(COPh)$_2$)$_3$]	-	-	-	1665(s) (νC=O), 1445(s) (νC=C)	This work
(Et$_4$N)$_2$[Mo(S$_2$C$_2$(COPh)$_2$)$_3$]	-	-	-	1662(s) (νC=O), 1450(s) (νC=C)	133
K$_4$[W$_2$O$_2$(μ-S)$_2$(CN)$_6$]	920(s)	-	470	2160(s), 2080(w) ν(C≡N)	This work

M = Mo, W; s = strong; m = medium; w = weak; S$_b$ = bridging sulfur.

Table 4.2. Infrared Spectral Data

Complex	ν(W=O) (cm^{-1})	ν(W$_{cent}$–S$_t$) (cm^{-1})	Other W–S vibrations (cm^{-1})
(Et$_4$N)$_2$[WO(WS$_4$)$_2$]	970(s)	–	490(m), 460(m), 435(w)
(PhCH$_2$Et$_3$N)$_2$[WO(WS$_4$)$_2$]	960(s)	–	500(m), 470(w), 450(w)
(2 Cl-CH$_4$Me$_2$NH)$_2$[WO(WS$_4$)$_2$]	955(s)	–	490(m), 470(w), 430(w)
(Et$_4$N)$_2$[WS(WS$_4$)$_2$]	–	530(m)	500(s), 490(m), 475(w), 440(w)
(Ph$_4$As)$_2$[WS(WS$_4$)$_2$]	–	525(m)	500(s), 490(m), 470(w)

s = strong; m = medium; w = weak.

Table 4.3.   Infrared Spectral Data

Complex	ν(M=O) (cm^{-1})	ν(M-S$_t$) (cm^{-1})	ν(S-S) (cm^{-1})	References
$[MoO(S_2)(S_2CNPr_2)]$	917(s)	–	555(m)	141
$Cs_2[MoO(S_2)_2(O_2CCOS)]$		–	530(m)	144, 145
$[WO(S_2)(S_2CNEt_2)_2]$	940(s)	–	552(m)	Present work
$[WO(S_2)(S_2CNPr_2)_2]$	945(s)	–	554(m)	Present work
$[WO(S_2)(S_2CN\hexagon)_2]$	940(s)	–	552(m)	Present work
$[WS(S_2)(S_2CNEt_2)_2]$	–	500(m)	545(m)	Present work
$[WS(S_2)(S_2CNPr_2)_2]$	–	500(m)	550(m)	Present work
$[WS(S_2)(S_2CN\hexagon)_2]$	–	500(m)	540(m)	Present work
$(Et_2NH_2)[WO(S_2)_2(S_2CNEt_2)]$	880(s)	–	540(m)	Present work
$(Pr_2NH_2)[WO(S_2)_2(S_2CNPr_2)]$	880(s)	–	535(m)	Present work
$[WO(S_2CNEt_2)_2]$	980(s)	–	–	Present work
$[WO(S_2CN\hexagon)_2]$	980(s)	–	–	Present work

M = Mo, W; s = strong, w = weak, m = medium, S_t= terminal sulfur.

Table 4.4. Infrared Spectra Data

Complex	$\nu(M=O)$ (cm^{-1})	$\nu(M-S_t)$ (cm^{-1})	$\nu(M-S_b)$ (cm^{-1})	Reference
$[Mo_2O_2(\mu-S)_2(S_2CNEt_2)_2]$	967, 952	-	477, 340	97
$[Mo_2OS(\mu-S)(S_2CNEt_2)_2]$	962, 956	544	471, 337	97
$[Mo_2S_2(\mu-S)(S_2CNEt_2)_2]$	-	548(m), 538(sh)	463, 334	97
$[W_2O_2(\mu-S)_2(S_2CNEt_2)_2]$	985(s), 970(sh)	-	470(m), 338(w)	Present work
$[W_2O_2(\mu-S)_2(S_2CN\bigcirc)_2]$	985(s), 975(sn)	-	465(m), 335(w)	Present work
$[W_2OS(\mu-S)_2(S_2CNEt_2)_2]$	980(s)	540(m)	465(m), 335(w)	Present work
$[W_2OS(\mu-S)_2(S_2CN\bigcirc)]$	980(s)	538(m)	460(m), 330(w)	Present work
$[W_2S_2(\mu-S)_2(S_2CNEt_2)_2]$	-	535(m), 535(sh)	460(m), 332(w)	Present work

M = Mo, W; s = strong; m = medium; w = weak; S_t = terminal sulfur; S_b = bridging sulfur.

Trinuclear clusters $[WO(WS_4)_2]^{2-}$ and $[WS(WS_4)_2]^{2-}$ show ν (W-O$_t$)and ν(W-S$_t$)of the central tungsten in the regions 955-970 cm^{-1} and 525-530 cm^{-1}, respectively. There are several other absorptions in the region 430-500 cm^{-1} arising from ν(W-S$_t$) and ν(W-S$_b$).Infrared spectra of this series of compounds are reproduced in Figs. 4.1.3 to 4.1.5 and data are tabulated in Table 4.2.

Other Ligand Vibrations

Dithiolene ligand vibrations

Cycloaddition of alkynes to the M-S-X unit is well documented in the literature.[76,77] Such reactions are not known with tungsten compounds. Here two activated acetylenes DBA (dibenzoylacetylene) and DMA (dimethylacetylene dicarboxylate) have been used to study this type of reaction with the tungsten-sulfur system. The detailed study on analogous molybdenum systems is well documented.[80] Amongst these, the most important is the insertion of DMA into Mo-S bond of the compound $(Et_4N)_2-[Mo_2O_2(\mu-S)_2(S_2)_2]$ [78], forming vinyl disulfide ligated compound. However, under refluxing conditions the vinyl disulfide compound rearranges to dithiolene isomer.[79] Reaction of $(Et_4N)_2[W_2O_2(\mu-S)_2(S_2)_2]$ with activated acetylenes has been carried out. Infrared spectra of these complexes are reproduced in Figs. 4.1.6 and 4.1.7. To distinguish the mode of insertion of the activated acetylenes across W-S or S-S bond of coordinated
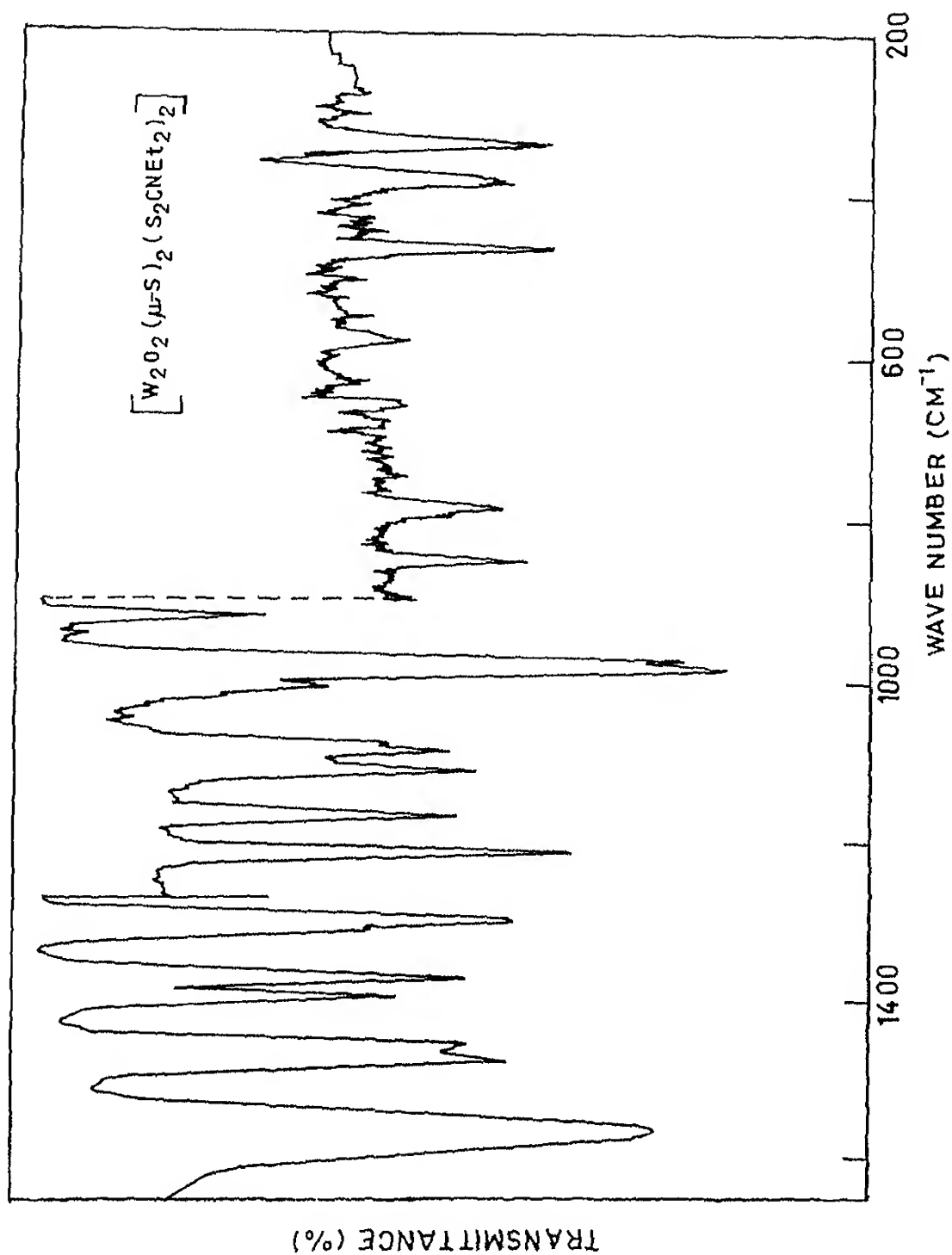
FIG 41.20 INFRARED SPECTRUM

$\left[W_2 O_2 (\mu\text{-}S)_2 (S_2 CNEt_2)_2 \right]$

WAVE NUMBER (CM^{-1})

TRANSMITTANCE (%)

100

$$\left[W_2 O_2 \; (\mu\text{-}S)_2 \; (S_2CN \bigcirc)_2 \right]$$

TRANSMITTANCE (%)

WAVE NUMBER (CM⁻¹)
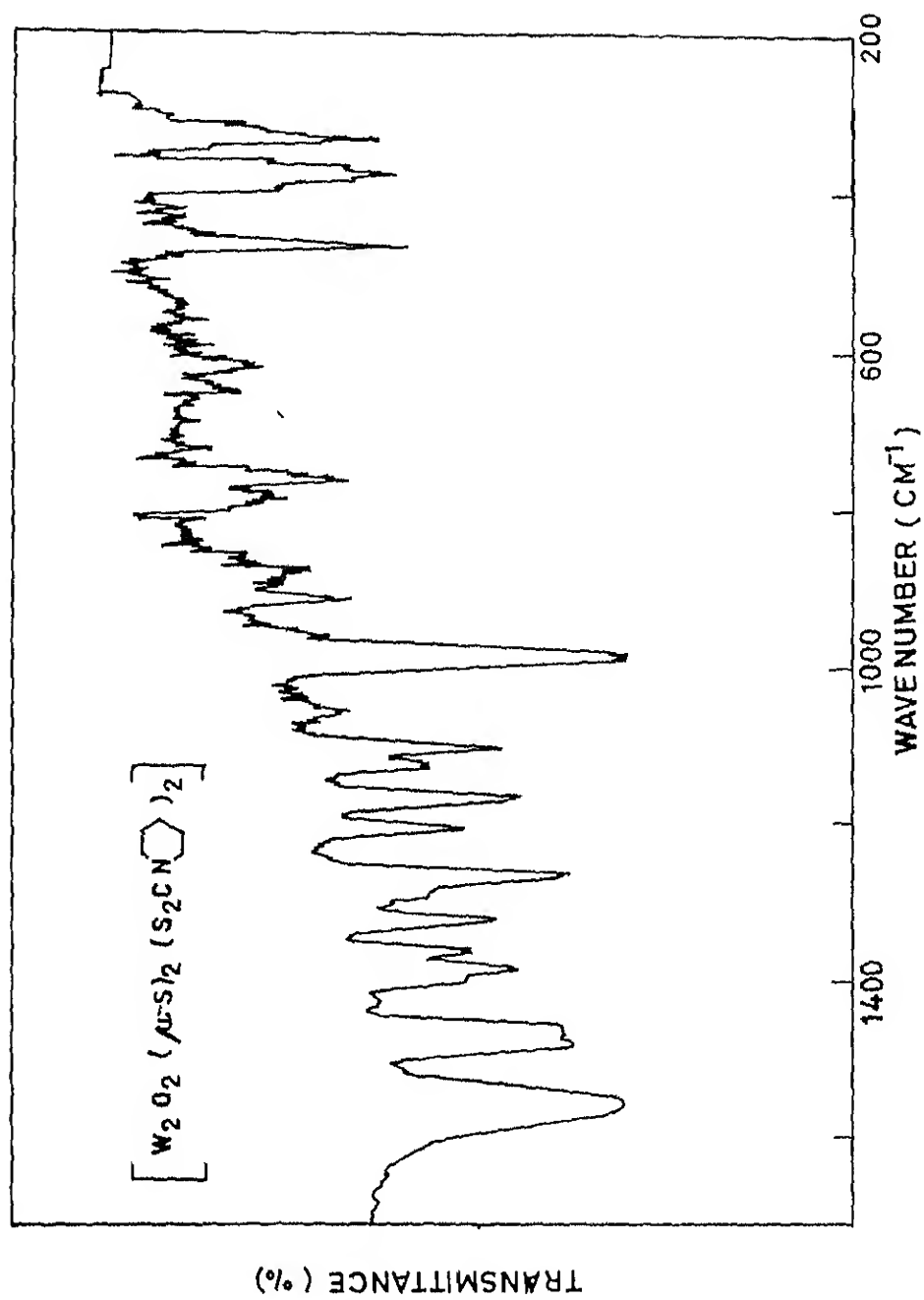
FIG. 4121 INFRARED SPECTRUM

101

$$\left[W_2 OS(\mu - S)_2 (S_2 CNEt_2)_2 \right]$$
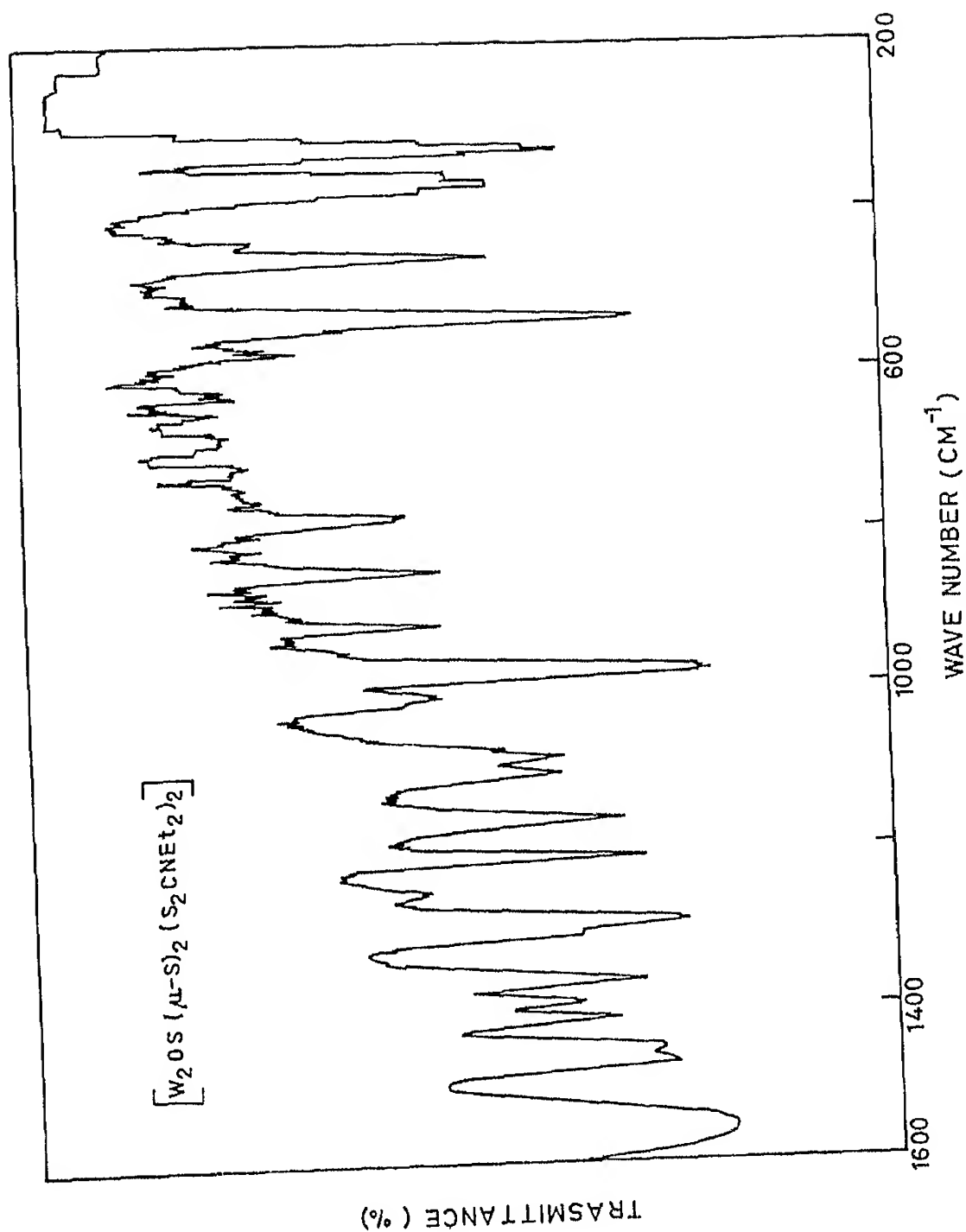
FIG. 4.1 22 INFRARED SPECTRUM

WAVE NUMBER (CM^{-1})

TRASMITTANCE (%)

$$\left[W_2OS \, (\mu\text{-}S)_2 \, (S_2CN\bigcirc)_2 \right]_2$$

WAVE NUMBER (CM^{-1})
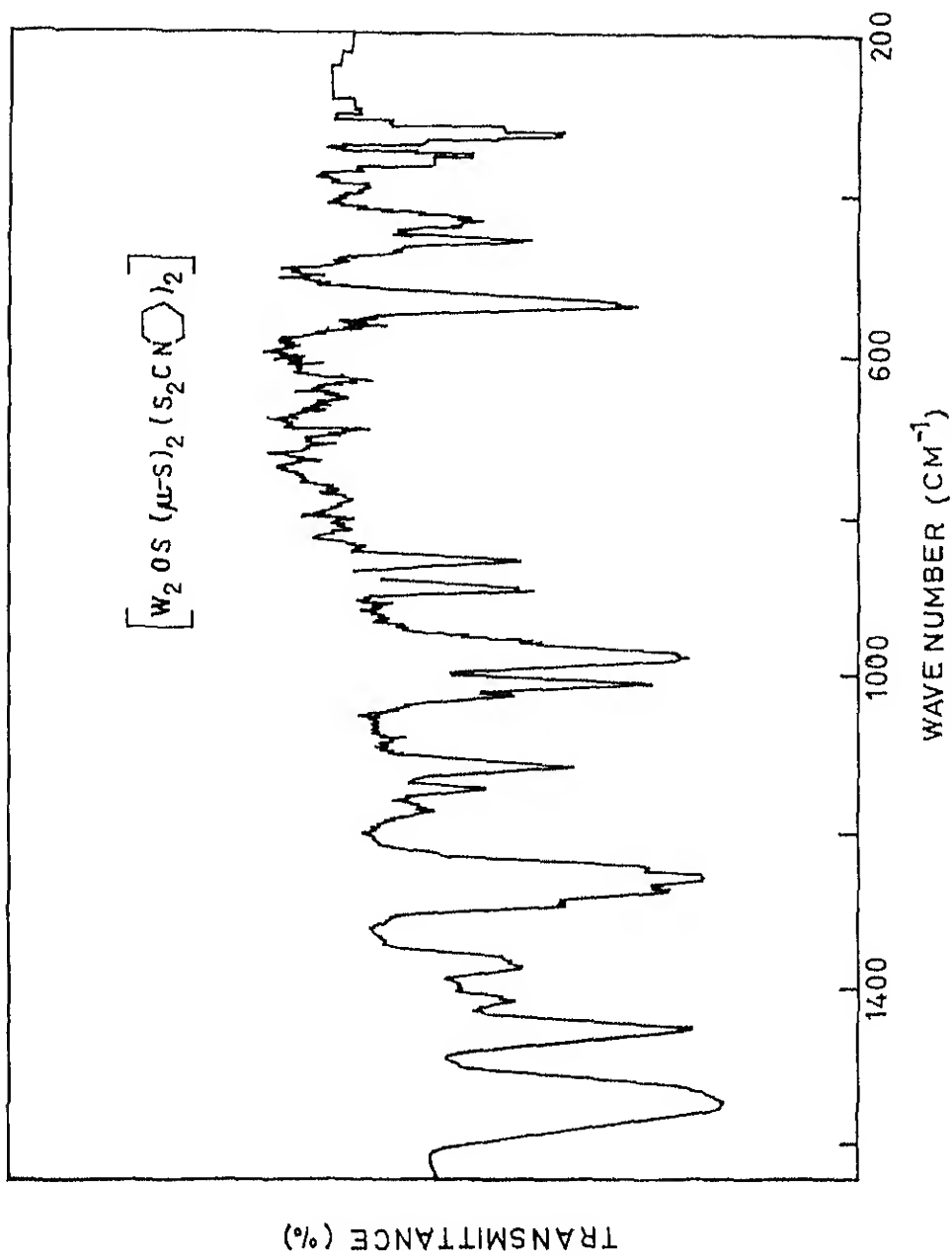
FIG 41.23 INFRARED SPECTRUM

$\left[W_2 S_2 (\mu\text{-}S)_2 (S_2CN Et_2)_2 \right]$

WAVE NUMBER (CM^{-1})

FIG. 4.1.24 INFRARED SPECTRUM

TRANSMITTANCE (%)

$S_2{}^{2-}$ ligand, IR spectra may be helpful if one can assign the presence of W-C bond in the vinyl disulfide complex. In the spectra of such complexes there are several vibrations in the low frequency region and the task of identifying such vibrations is not possible. For the dithiolene complexes C=C stretching frequency could be a rough measure of C=C bond strength. This stretching frequency is mainly dependent on the nature of the substituent group on the carbon atoms. Thus, to distinguish vinyl disulfide or dithiolene mode of coordination of the insertion reaction, ν (C=C) could help in understanding the mode of reaction. The infrared spectral data presented in Table 4.1 for the complexes reported here suggest that ν (C=C) appears in the range where the substituent groups on carbon are sulfur along with functional group (-COPh or -COOMe) and there is n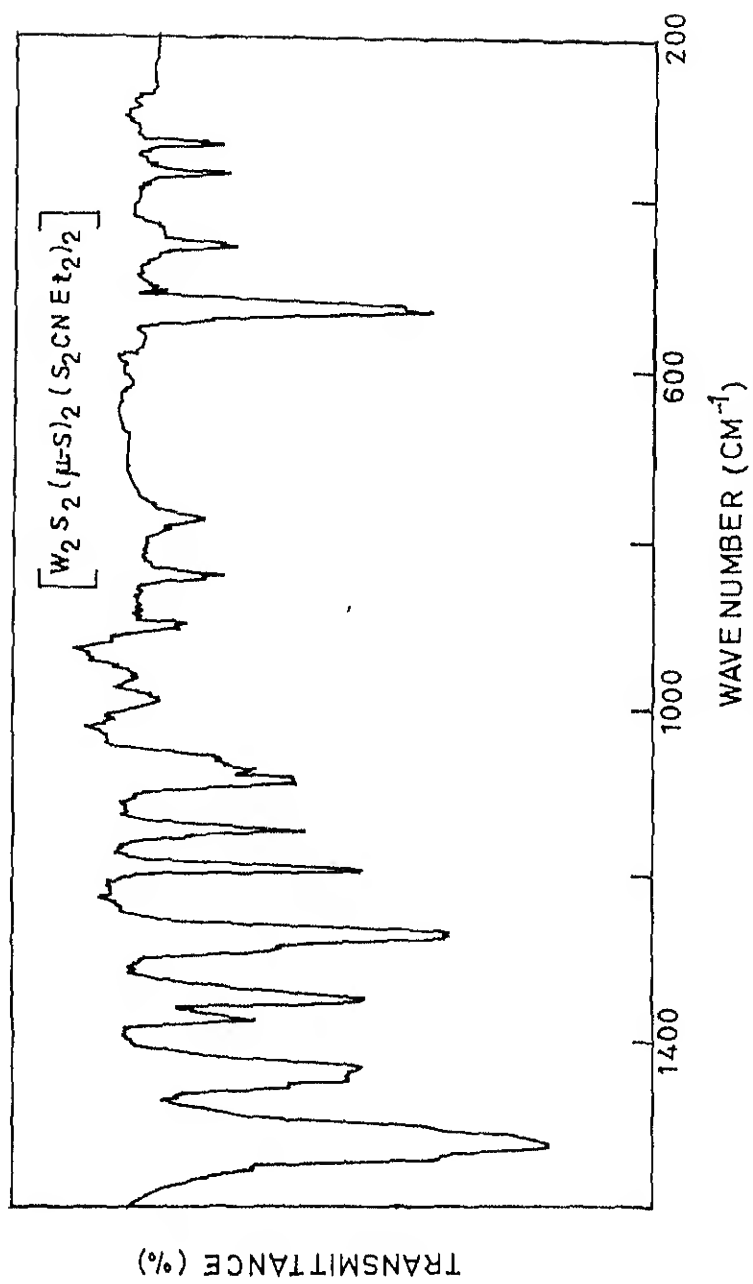o dramatic change in this frequency when compared to other dithiolene complexes. Thus, we can tentatively assign the formation of dithiolene ligand formation instead of vinyl disulfide formation which has been established by ^{13}C NMR studies (vide infra). The assignment of ν (W-S) vibration arising from dithiolene coordination is going to be difficult as they are often strongly coupled with π-ring vibrations of the ligand.[143] Thus a serious discussion in this regard is not possible.

The spectra of other dithiolene complexes of tungsten reported here are presented in Figs. 4.1.6 to 4.1.8 and important assignments are made by comparing the spectra of the corresponding molybdenum analogs (Table 4.1).

Infrared spectra of cyanosubstituted complex $K_4[W_2O_2(\mu-S)_2-(CN)_6].3H_2O$ shows $\nu(CN)$ at 2075(s) and 2070(w) cm^{-1} (Fig. 4.1.9) which is slightly more than the free cyanide.[146] It is difficult to assign $\nu(W-C)$ in this complex, as there are some other vibrations arising from $\nu(W-S_b)$. However, a tentative assignment can be made by comparing it with other similar complexes where no metal-carbon bond is involved. Proceeding in this direction, vibration at 450 cm^{-1} may be attributed to $\nu(W-S_b)$ and rest of the vibrations at 420, 335 and 310 cm^{-1} can reasonably be assigned to $\nu(W-C)$.

Many of the complexes synthesized here, have dialkyl dithiocarbamate ligand attached to the metal. Spectra of similar complexes have been studied extensively. Mode of coordination of this ligand can be understood by monitoring the splitting of $\nu(C-S)$ near 1000 cm^{-1} and the appearance of $\nu(CN)$ in the region 1450-1600 cm^{-1}.[147] Infrared stretching frequencies for such complexes which appear above 1500 cm^{-1} suggest that dithiocarbamate acts as a bidentate ligand. The $\nu(W-S_{dtc})$ appears in the region 400-300 cm^{-1} which is mixed with some other vibrations, some times. Thus, the correct assignment of $\nu(W-S_{dtc})$ is not straightforward except in the case of $[WO(S_2CNR_2)_2]$ where it appears at 355, 340 and 320 cm^{-1} (R = Et).

4.2.2 Electronic Spectra

The electronic absorption spectra of $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ ion and other persulfido complexes are reproduced in Figs. 4.2.3,
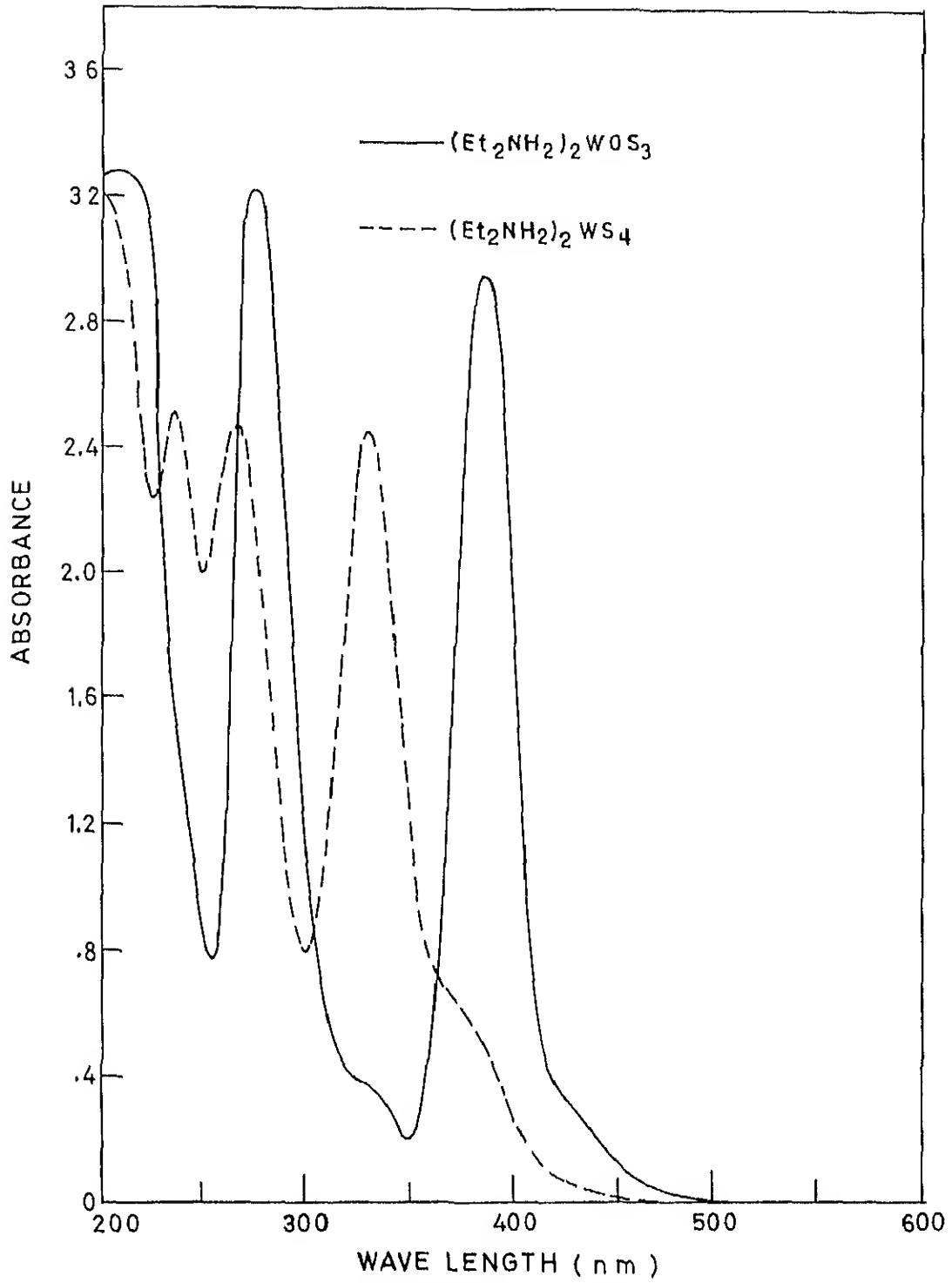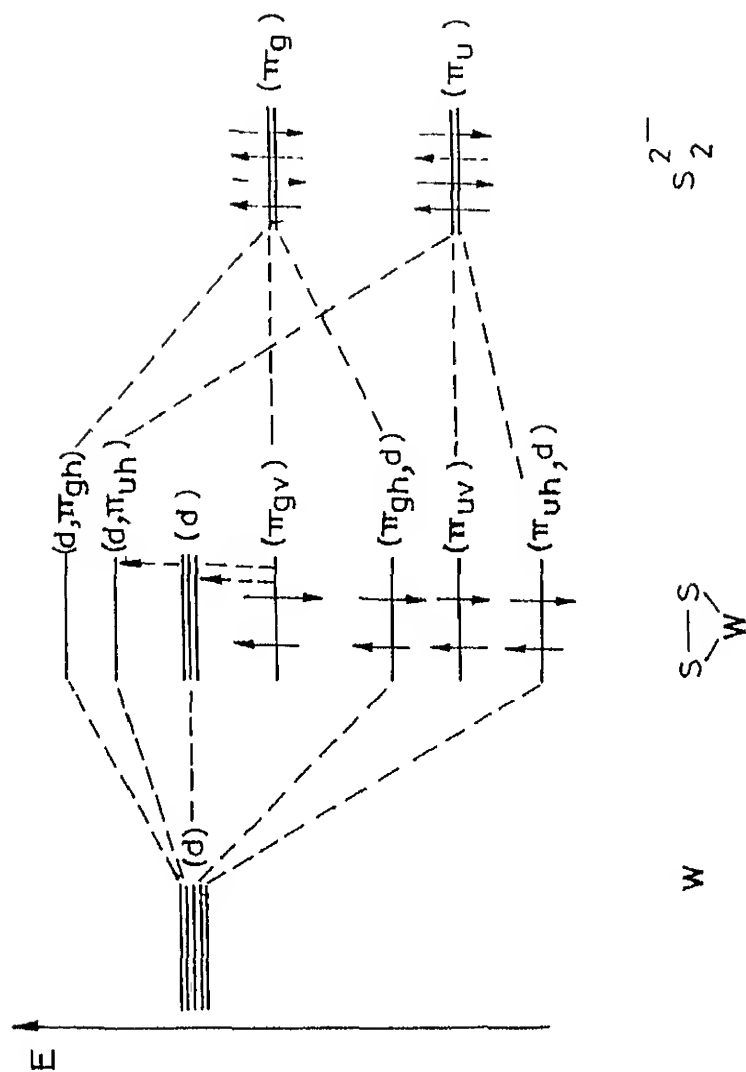
FIG 4 2.1   ELECTRONIC SPECTRA

FIG 4.2.2   QUALITATIVE MO SCHEME FOR PERSULFIDO COMPLEXES

4.2.9 to 4.2.11. The electronic absorption maxima and the corres-

ponding extinction coefficients for these complexes are tabulated

in Table 4.5 and 4.6. When $S_2{}^{2-}$ is bonded in side on $(\eta)^2$ fashion

to a metal, the $\pi*$ orbital of $S_2{}^{2-}$ splits into strongly inter-

acting $\pi_h{}^*$ orbital in the $\{M\overset{S}{\underset{S}{\lessgtr}}\}$ plane and a weakly interacting

$\pi_v{}^*$ orbital perpendicular to the $\{M\overset{S}{\underset{S}{\lessgtr}}\}$ plane. The longest wave

length band in $[MoO(S_2)(S_2CNEt_2)_2]$ occurs around 580 n.m. and is

assigned to a LMCT (ligand to metal change transfer) of the type

$\pi_v{}^*$ (S) $\rightarrow$ d(Mo).[150] This assignment has been taken valid for

the complex ion, $[Mo_2O_2(\mu-S)_2(S_2)_2]^{2-}$ where molybdenum is still

in the high oxidation state.[86] The position of these bands is

affected by several factors for example, the oxidation state of

the metal, the presence of other ligands and the involvement of

metal-metal bond in dimeric complexes. These factors determine

the energy of LUMO and its metal character. A qualitative MO

scheme for $\{M\overset{S}{\underset{S}{\lessgtr}}\}$ moiety (side on coordination bond symmetry C_{2v})

is shown in Fig. 4.2.2. This MO scheme is similar to the one

developed for dioxygen metal complexes.[150,151]

For the complex ion, $[Mo_2O_2(\mu-S)_2(S_2)_2]^{2-}$ the assignments

of absorption bands are according to the discussion mentioned

above. Thus, the lowest energy band around 460 n.m. is assigned

to $\pi_v{}^*$ (S) $\rightarrow$ d(Mo) (LMCT) and a relatively weak band around

377 n.m. has been assigned to $\sigma \rightarrow \sigma*$ charge transfer arising

from Mo-Mo bonding. This is consistent with Mo-Mo bond distance

and the diamagnetic nature of the compound.[86] The high energy

$\epsilon \left[10^3 \check{M}^1 cm^1 \right]$

ABSORBANCE

——— $(Me_4N)_2 \left[W_2 O_2 (\mu-S)_2 (S_2)_2 \right]$

- - - - $(Et_4N)_2 \left[W_2 O_2 (\mu-S)_2 (S_2)_2 \right]$

WAVE LENGTH (nm)

FIG 4 2.3   ELECTRONIC SPECTRA

Legend:
— $(Et_4N)_2[WS(WS_4)_2]$
--- $(Ph_4AS)_2[WS(WS_4)_2]$
-·-·- $(Et_4N)_2[WO(WS_4)_2]$

OPTICAL DENSITY

WAVE LENTH (nm)

FIG 4.2.4   ELECTRONIC SPECTRA

ABSORBANCE

$(C_6H_5 \ CH_2(C_2H_5)_3N)_2[W_3OS_8]$

$(Cl \ C_2H_4(CH_3)_2NH)_2[W_3OS_8]$

300   500   700

WAVE LENGTH (nm)
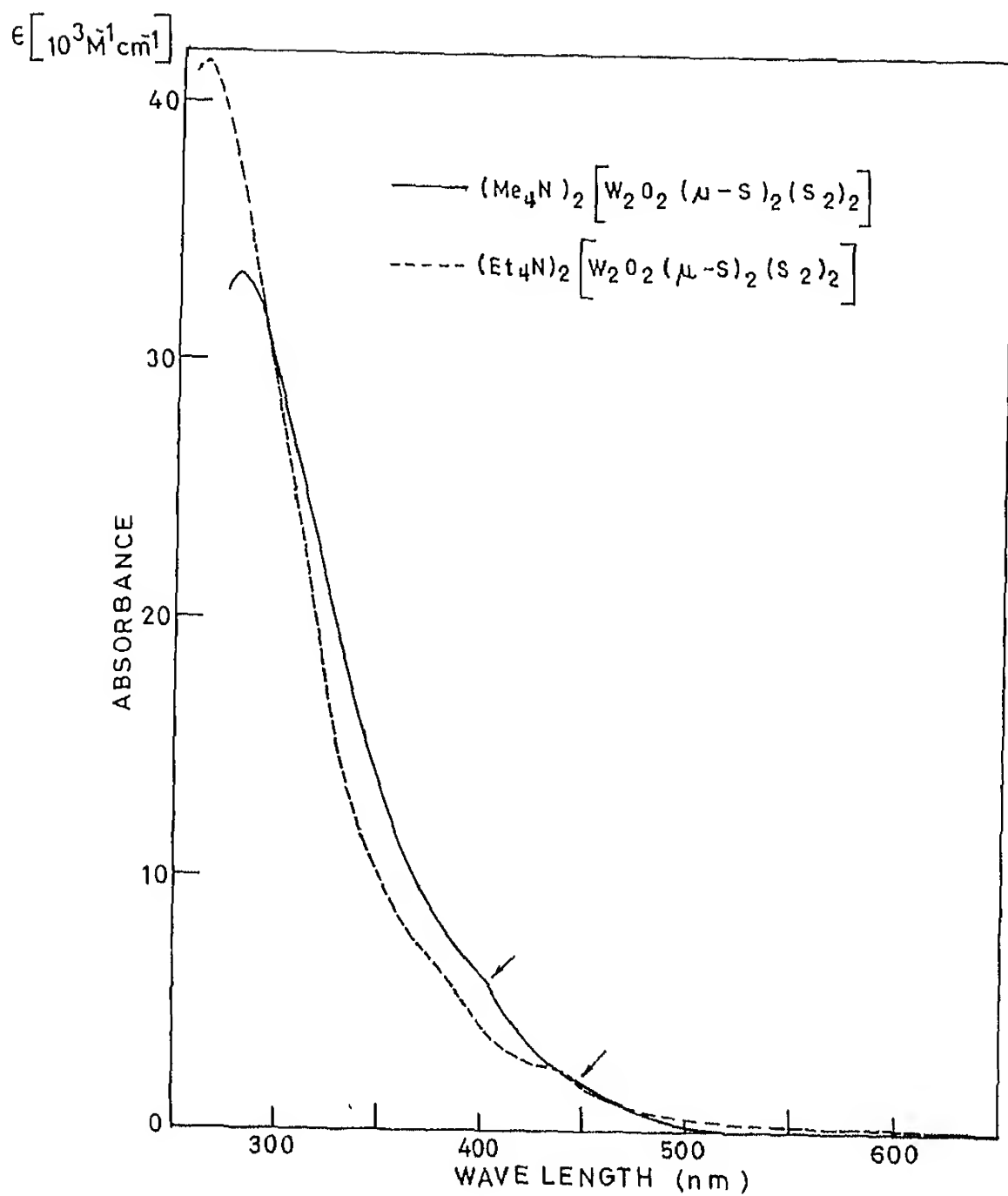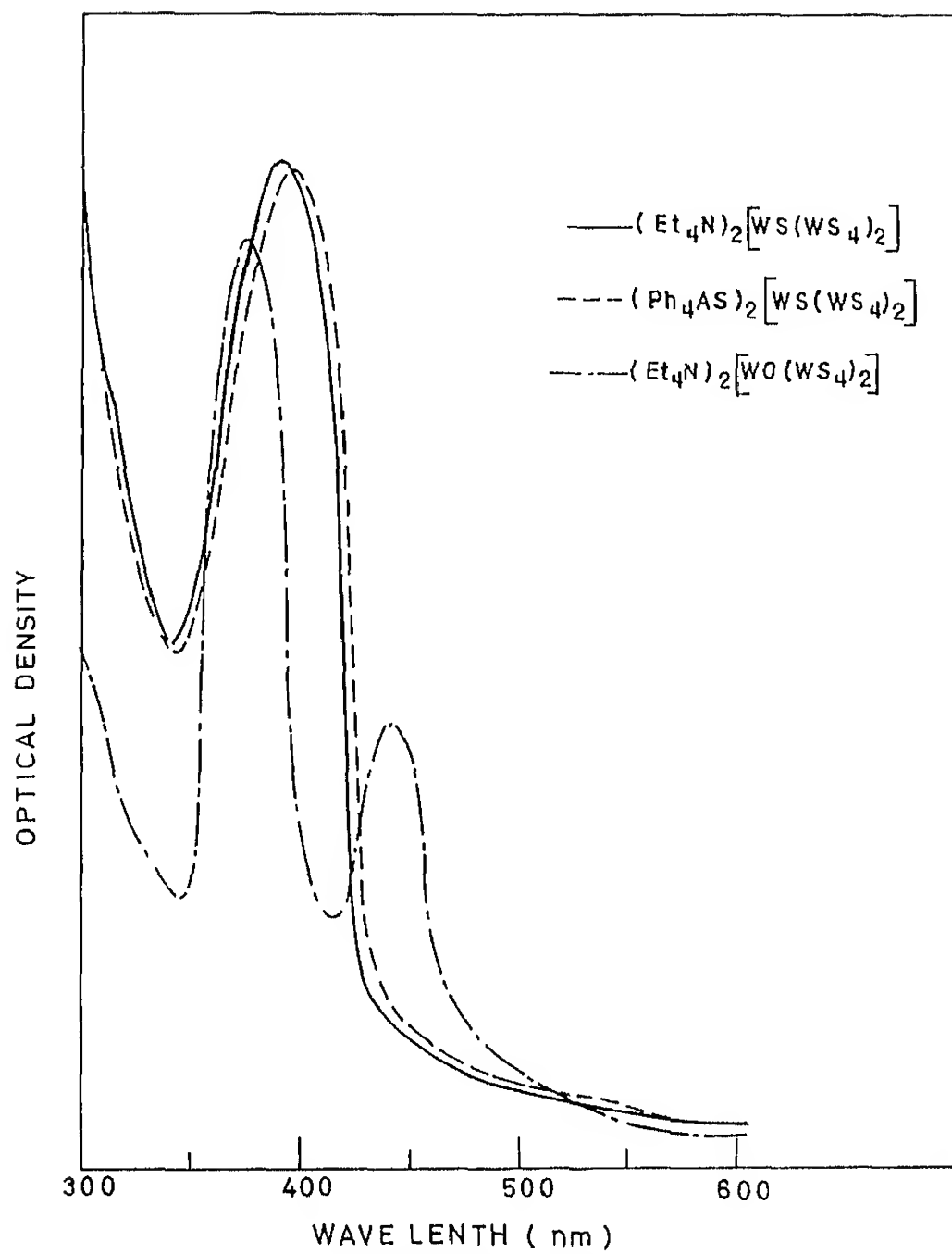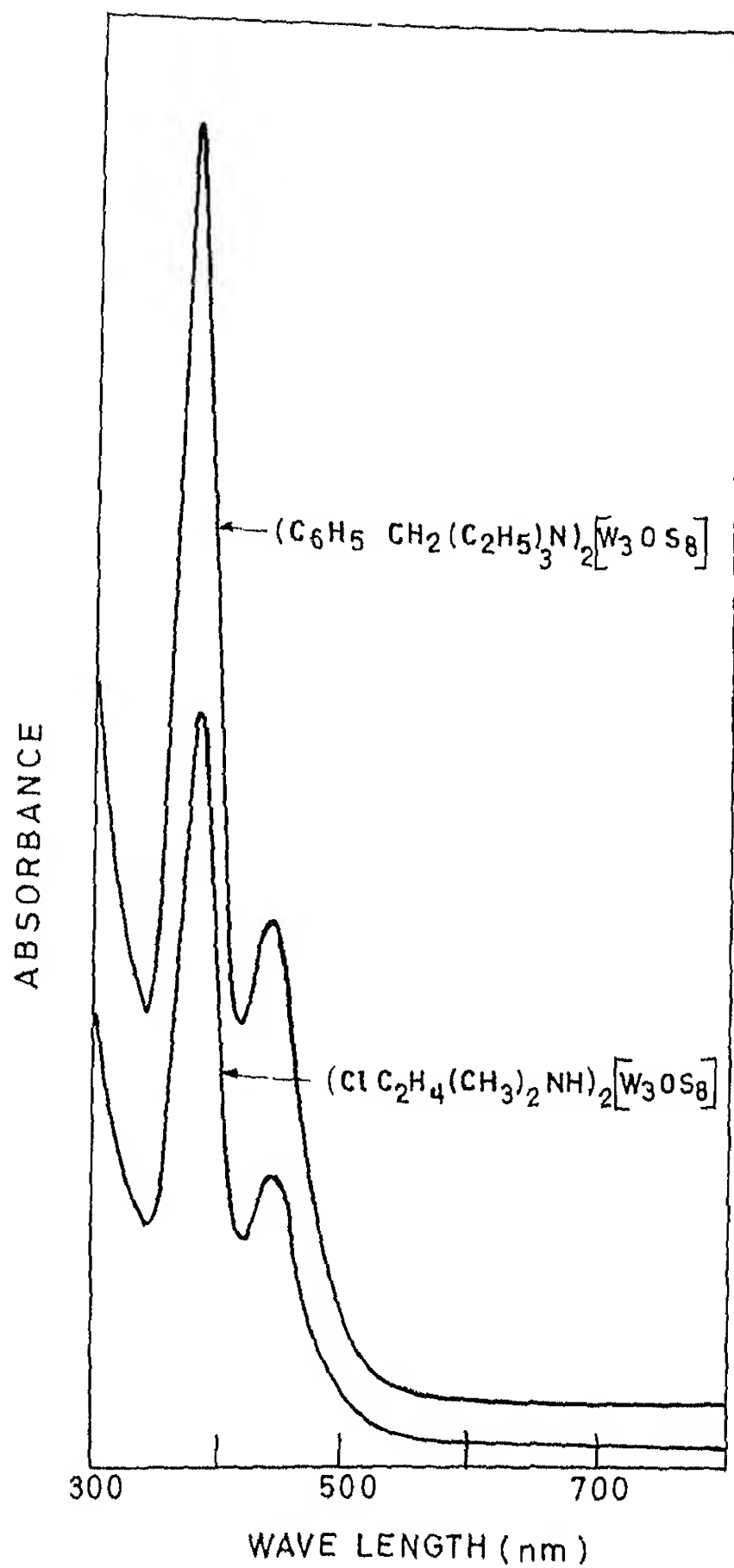
FIG. 4.2.5   ELECTRONIC SPECTRA
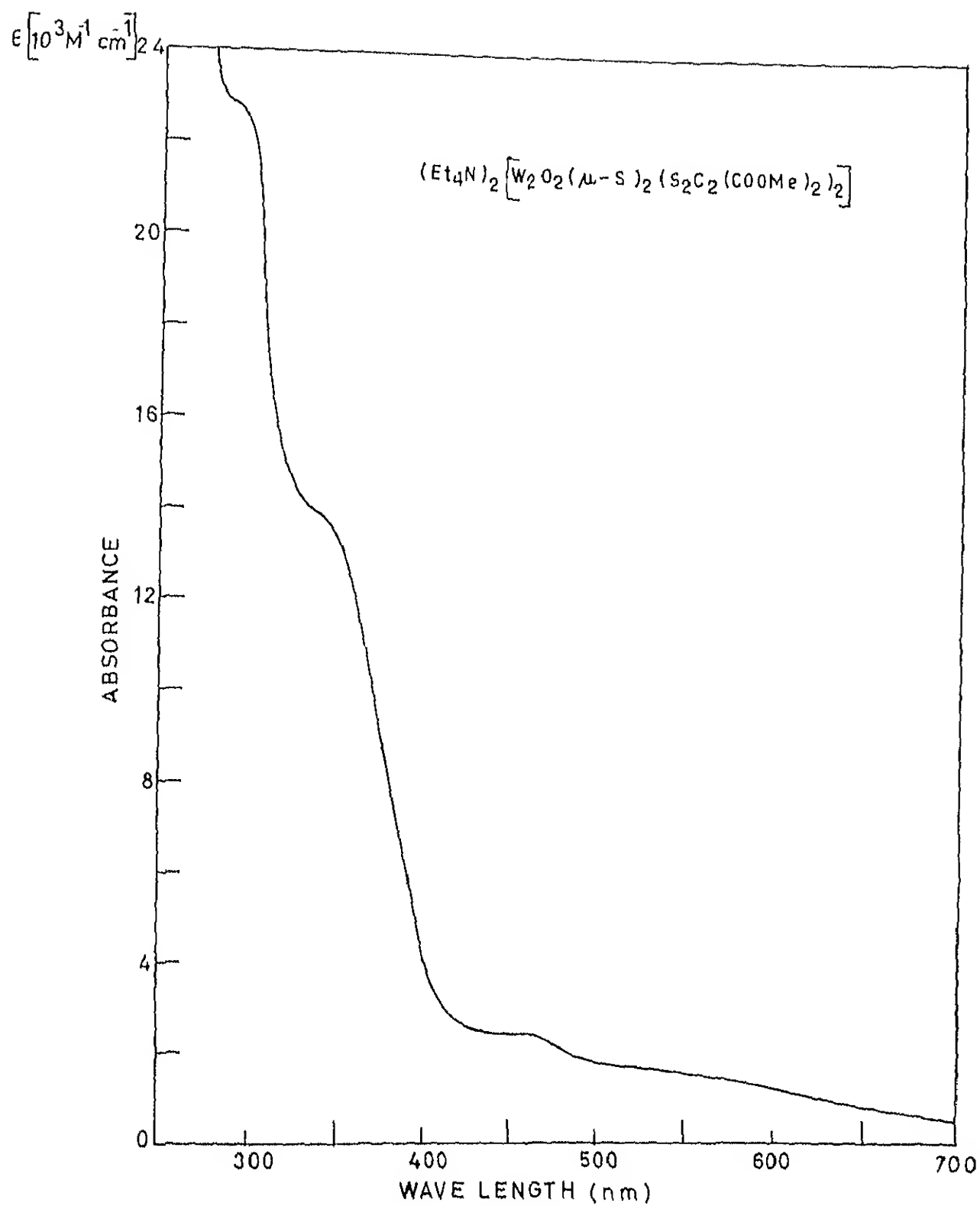
FIG 4.2.6 ELECTRONIC SPECTRUM
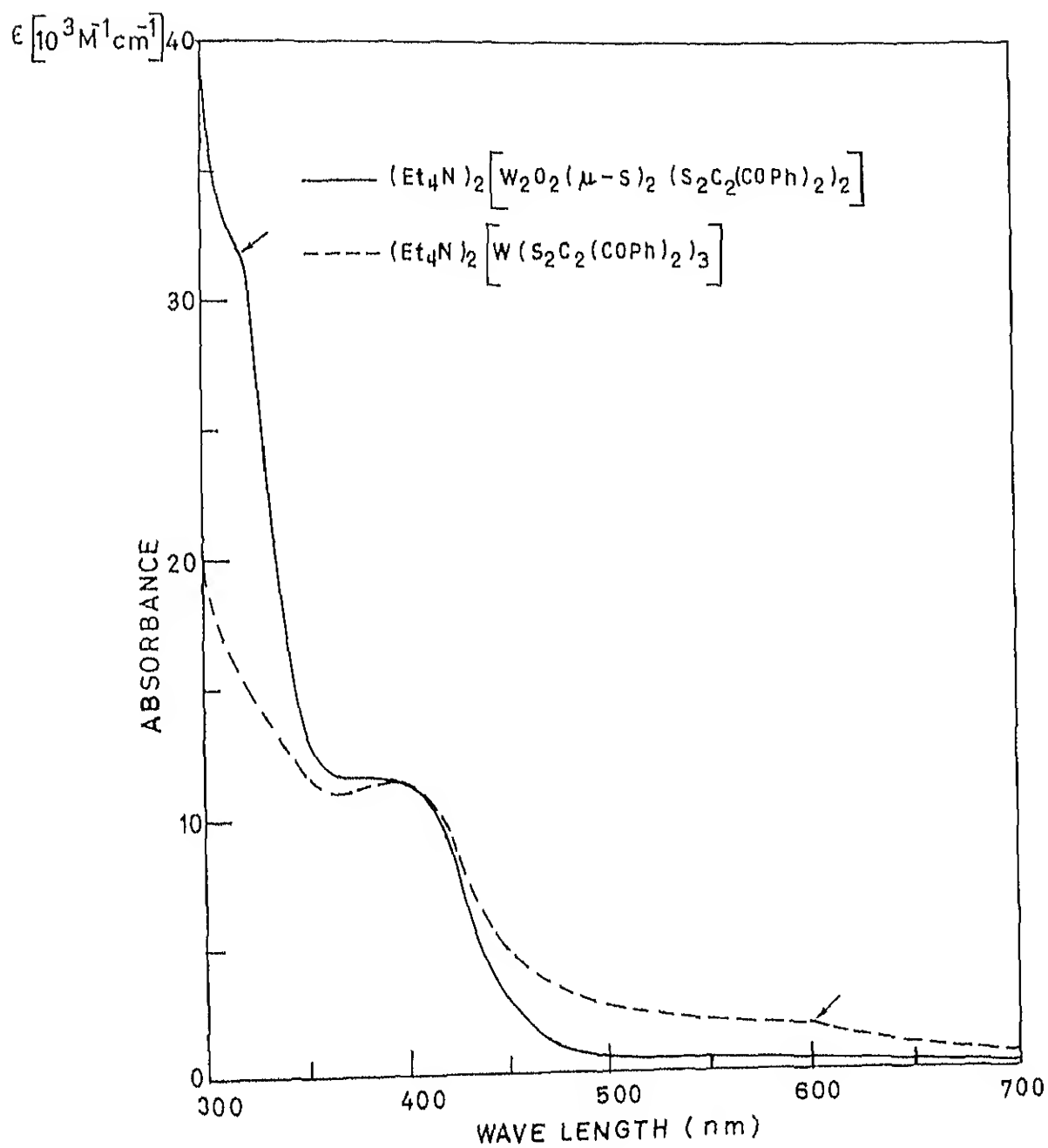
FIG 4.2.7   ELECTRONIC SPECTRA

FIG 4.28   ELECTRONIC SPECTRUM

$\epsilon\left[10^3 M^{-1} cm^{-1}\right]$

16

12

8

4

ABSORBANCE

———— $\left[WO(S_2)(S_2CNEt_2)_2\right]$

------- $\left[WO(S_2)(S_2CNPr_2)_2\right]$

— — — $\left[WO(S_2)(S_2CN\bigcirc)_2\right]$

300   400   500   600   700
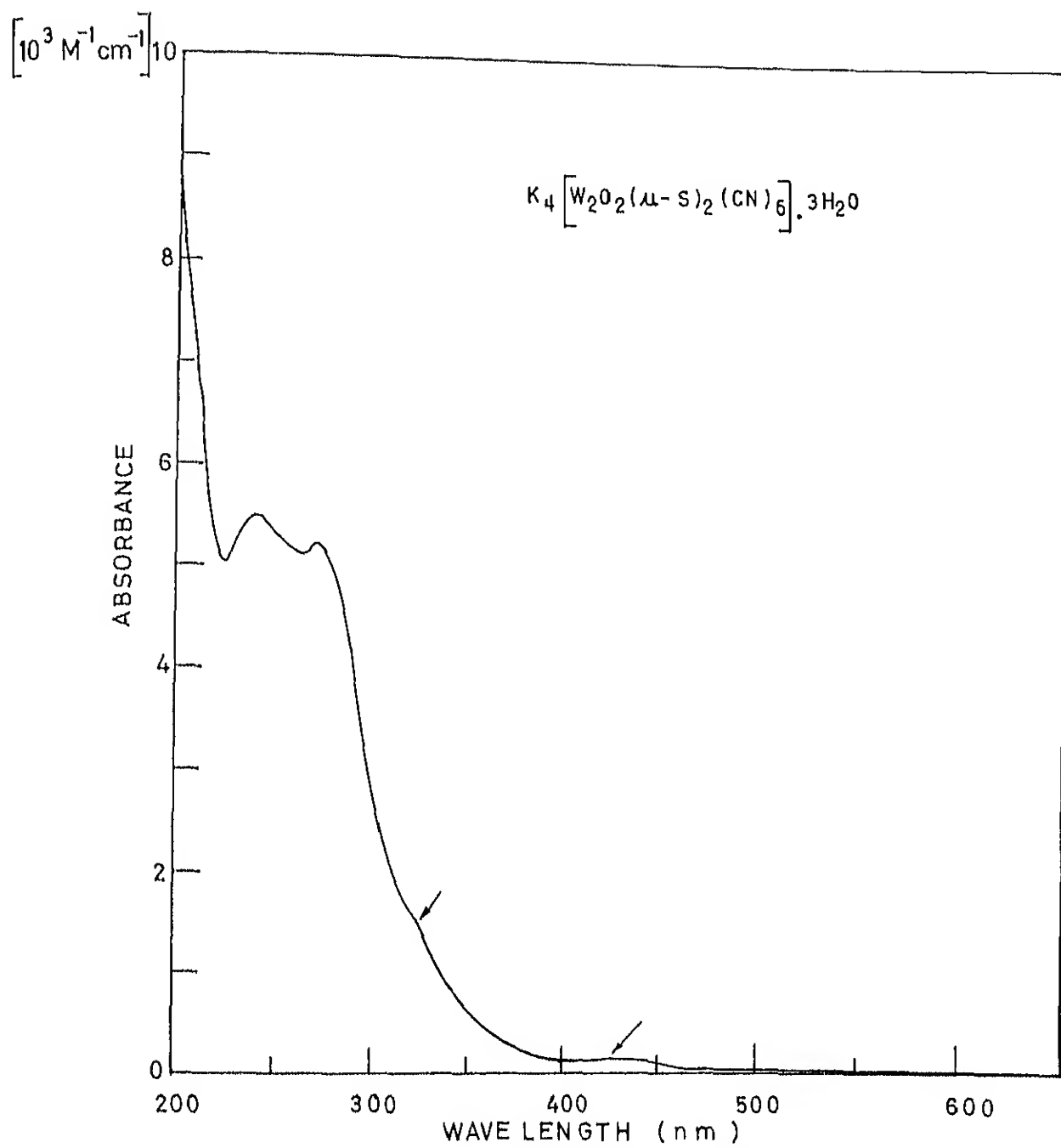
WAVE LENGTH (nm)
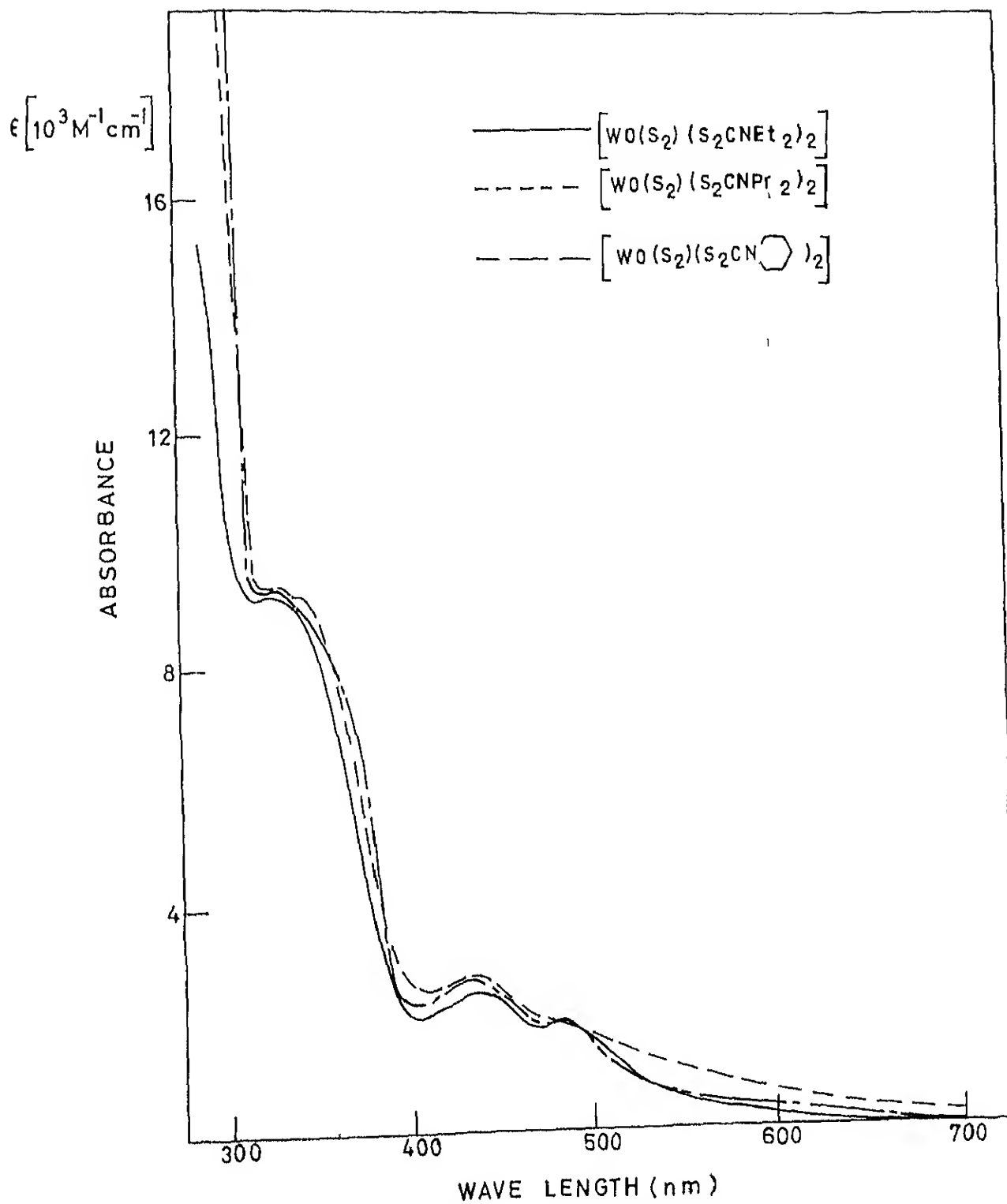
FIG 4.2.9   ELECTRONIC   SPECTRA

$\epsilon \left[10^3 \text{M}^{-1}\text{cm}^{-1}\right]$

WS(S$_2$)(S$_2$CNEt$_2$)$_2$

WS (S$_2$)(S$_2$CNPr$_2$)$_2$

WS (S$_2$) (S$_2$CN◯)$_2$

16

12

8

4

0

ABSORBANCE

300   400   500   600   700

WAVE LENGTH (nm)

FIG. 4 2 10   ELECTRONIC SPECTRA

$\epsilon \left[10^3 \, \text{M}^{-1} \text{cm}^{-1} \right]$

ABSORBANCE

WAVELENGTH (nm)

(Et$_2$NH$_2$) $\left[\text{WO}(S_2)_2 (S_2\text{CNEt}_2) \right]$

(Pr$_2$NH$_2$) $\left[\text{WO}(S_2)_2 (S_2\text{CN Pr}_2) \right]$

FIG 4.2 11   ELECTRONIC SPECTRA

bands in u.v. region are assigned to charge transfer originating from sulfido group to metal center and $\pi \rightarrow \pi*$ transition of $\{Mo{<}^{S}_{S}|\}$ moiety.[86]

For the complex ion, $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ a similar argument can be put forward to assign the electronic transitions because this complex is isostructural to its molybdenum analog (X-ray powder pattern vide 4.5.7) and shows similar diamagnetic behaviour. Thus, the red colour of $(Et_4N)_2[W_2O_2(\mu-S)_2(S_2)_2]$ is due to the transition of the type $\pi_v^*(S) \rightarrow d(W)$ which appears around 430 n.m. The second band around 380 n.m. which appears as shoulder, is relatively weak in nature and may be due to $\sigma \rightarrow \sigma*$ transition originating from W-W bonding. The high energy u.v. band at 260 n.m.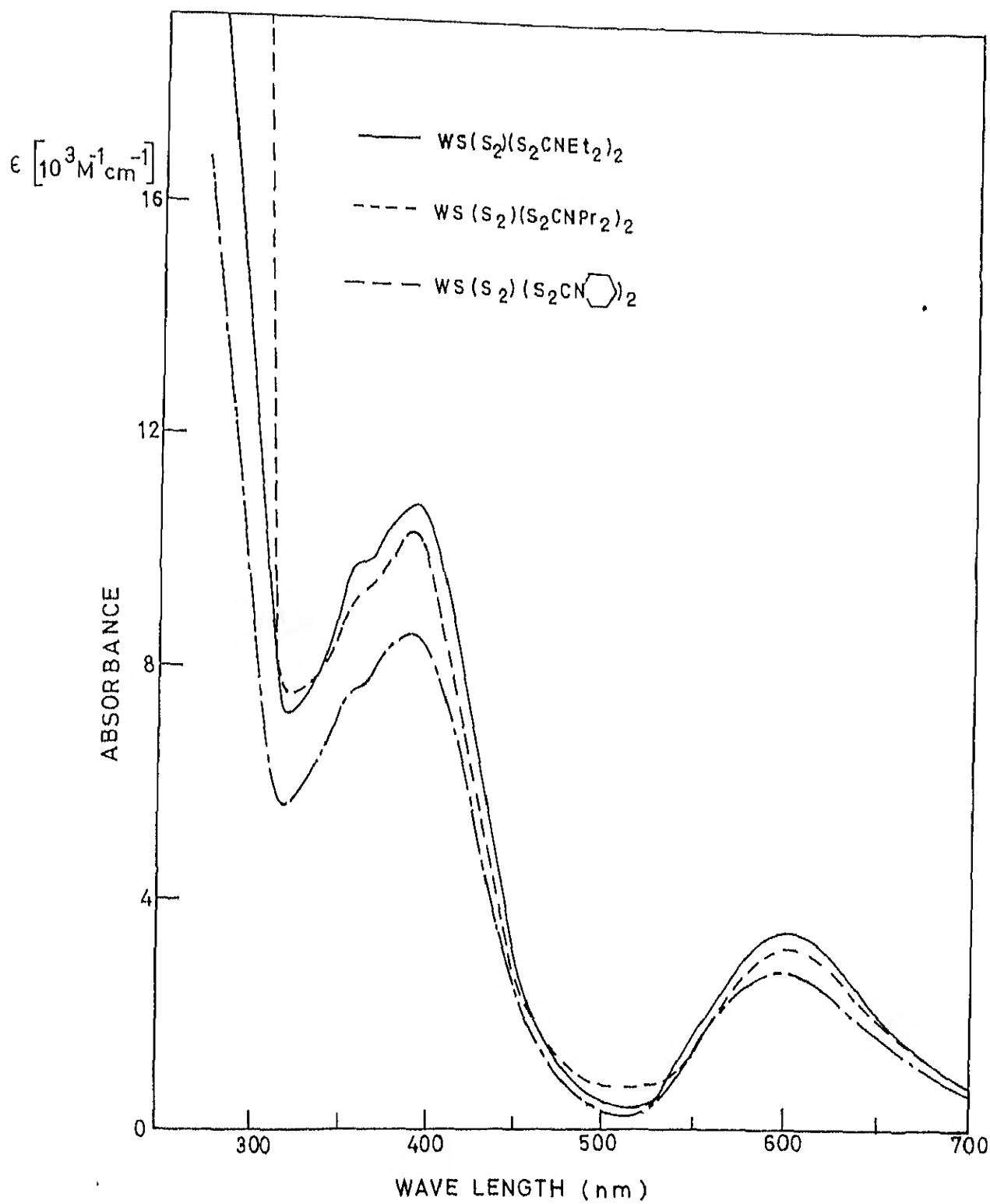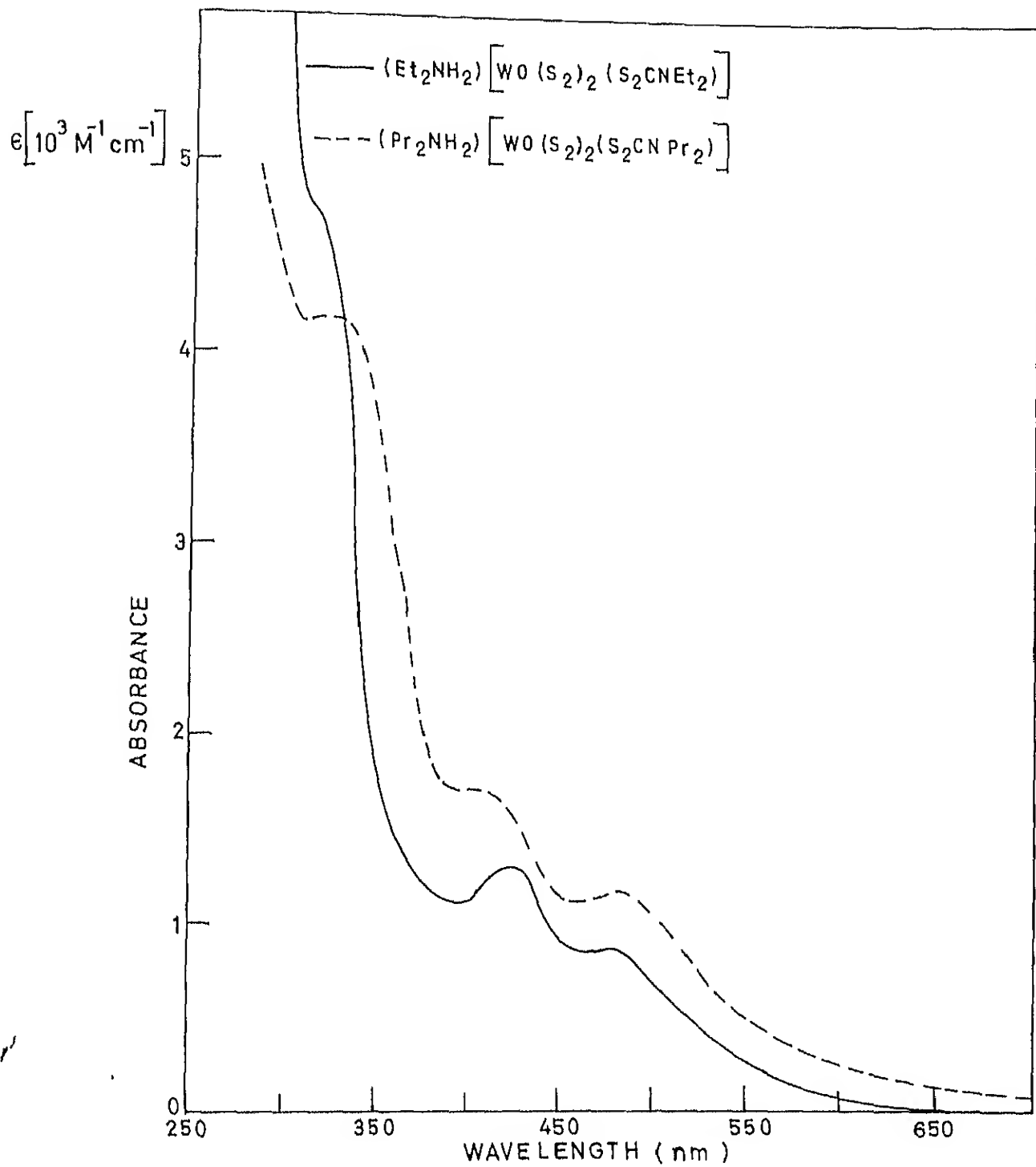 is then due to charge transfer from bridging sulfur to tungsten and/or $\pi \rightarrow \pi*$ transition in $\{W{<}^{S}_{S}|\}$ moiety. Salts of the ion $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ are not stable enough to carry out Resonance Raman study. Hence any confirmation of these electronic transitions could not be done.

In case of the complexes of the type $[WO(S_2)(S_2CNEt_2)_2]$, the arguments given above for $\{W{<}^{S}_{S}|\}$ moiety should be valid, considering the presence of the coligand, dithiocarbamate. The electronic spectrum of free dithiocarbamate exhibits three bands in the u.v. region and on complexation, the shift in these bands are not significant.[139,140] The nature of these transitions is intraligand: $n \rightarrow \pi*$, $\pi \rightarrow \pi*$ and $n \rightarrow \sigma*$. Keeping this in mind, the high energy bands in the u.v. region could be assigned to dithiocarbamate intraligand transitions.

Comparing the corresponding molybdenum complex, the longest wave length band at 480 n.m. for $[WO(S_2)(S_2CNR_2)_2]$ is assigned to $\pi_v^*(S) \longrightarrow d(W)$ transition. The second band around 435 n.m. could be due to $\pi_{gv} \longrightarrow \pi_{uh}$ charge transfer of the $\{W \overset{S}{\underset{S}{\diagdown\diagup}}|\}$ moiety. Both of these transitions are ligand to metal charge transfer type. The extinction coefficient values of these two transitions support this assignment because the first transition takes place into an empty metal d-orbital and the second to the antibonding MO which is predominantly metal in character. If the transitions originate from (π_{gh}, d) and $\pi_{uh}, d)$ orbitals to the antibonding orbitals (d, π_{uh}) and (d, π_{gh}), the extinction coefficient should be high.[150]

For the compounds of the type $[WS(S_2)(S_2CNR_2)_2]$ the highest energy band around 360 n.m. is due to intraligand charge transfer transition of dithiocarbamate ligand. The lowest energy band is then assigned to $\pi_v^*(S) \longrightarrow d(W)$ transition. However, the middle band at 390 n.m. has a very high extinction coefficient. The corresponding oxo analog shows a band at 435 n.m. with low extinction coefficient. The position of this band at 390 n.m. compared to 435 n.m. for the oxo analog and its intense nature suggests that the origin of this transition may be of the type $(\pi_{gh}, d)/(\pi_{uh}, d) \longrightarrow (d, \pi_{uh})/d, \pi_{gh})$.

The electronic absorption spectrum of $(R_2NH_2)[WO(S_2)_2-(S_2CNR_2)]$ is similar to that of $[WO(S_2)(S_2CNR_2)_2]$. By following the arguments stated above, the bands around 475, 415 and 310 n.m.

can be assigned to π_v^* (S) $\rightarrow$ d(W), $\pi_{gv} \rightarrow \pi_{uh}$ and intraligand

charge transfer transitions, respectively.

Electronic absorption spectra of dinuclear dithiocarbamato

tungsten(V) complexes are reproduced in Figs. 4.2.13 and 4.2.14.

Lozano and coworkers have isolated similar complexes with diffe-

rent bulky substituents on dithiocarbamate, following a multistep

process.[139,140] They could observe very weak d-d transitions

because of the appreciable solubility of their complexes. The

diethyl and piperidine dithiocarbamates used here, give similar

tungsten complexes, which have unfortunately restricted solubility.

Thus, the expected d-d transition could not be selected. The spectra

of this series of complexes are predominantly charge transfer type.

A comparison of the electronic spectrum of free dialkyl dithio-

carbamate with the electronic spectra of these complexes suggests

that the high energy u.v. bands are originating from the coordinat-

ed dithiocarbamate ligand. There is only one absorption in the

visible region ranging from 415 to 422 n.m. which may be assigned

to charge transfer transition from ligand (bridged disulfide and/

or dithiocarbamate ligand) to tungsten.

The electronic spectra of dithiolene ligated complexes

containing $\{W_2^V O_2 (\mu-S)_2\}^{2+}$ core, recorded in the range 700-300 n.m.

exhibit only two transitions (Fig. 4.2.6 and 4.2.7). There are

dramatic changes in the band position as well as their extinction

coefficient values, with the change of the substituent group in

$S_2C_2R_2^{2-}$ (R = COPh, COOMe, Table 4.5). Similar observations have

FIG. 4.2.12 ELECTRONIC SPECTRA

$\epsilon\left[10^3 M^{-1} cm^{-1}\right]$

1. $\left[W_2 O_2 (\mu-S)_2 (S_2CNEt_2)_2\right]$

2. $\left[W_2 O S (\mu-S)_2 (S_2CNEt_2)_2\right]$

3. $\left[W_2 S_2 (\mu-S)_2 (S_2CNEt_2)_2\right]$
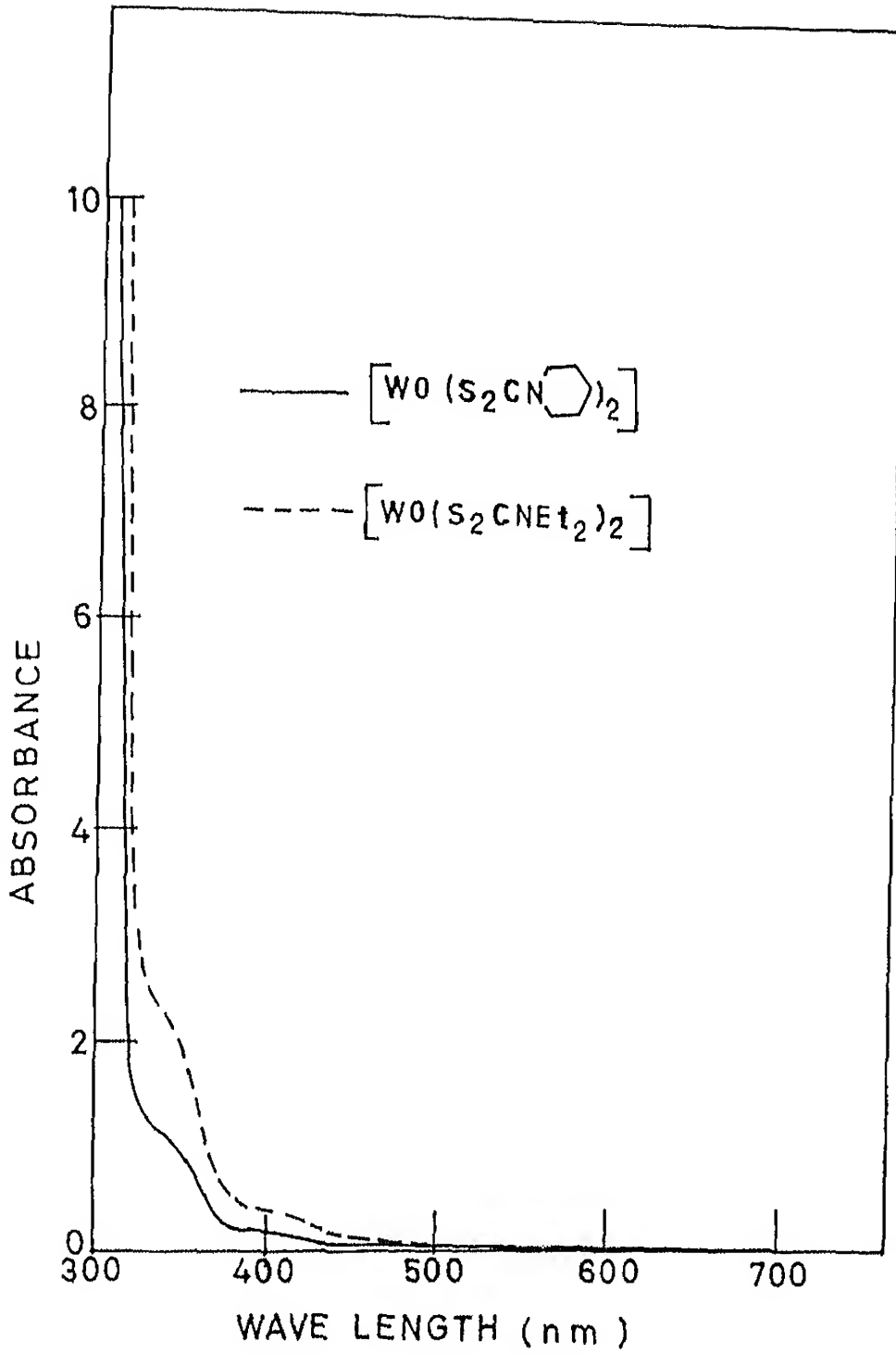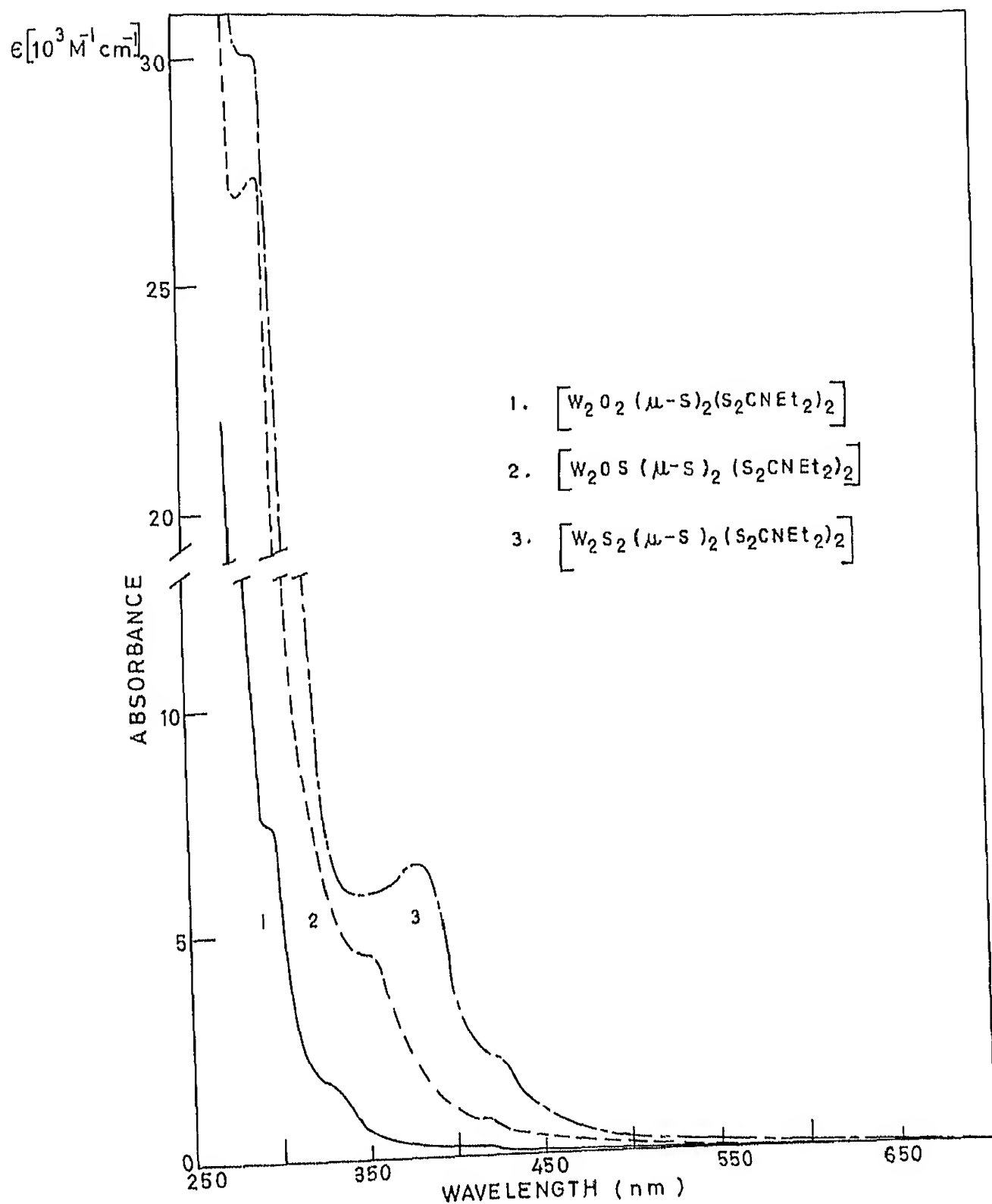
FIG. 4 2 13   ELECTRONIC SPECTRA
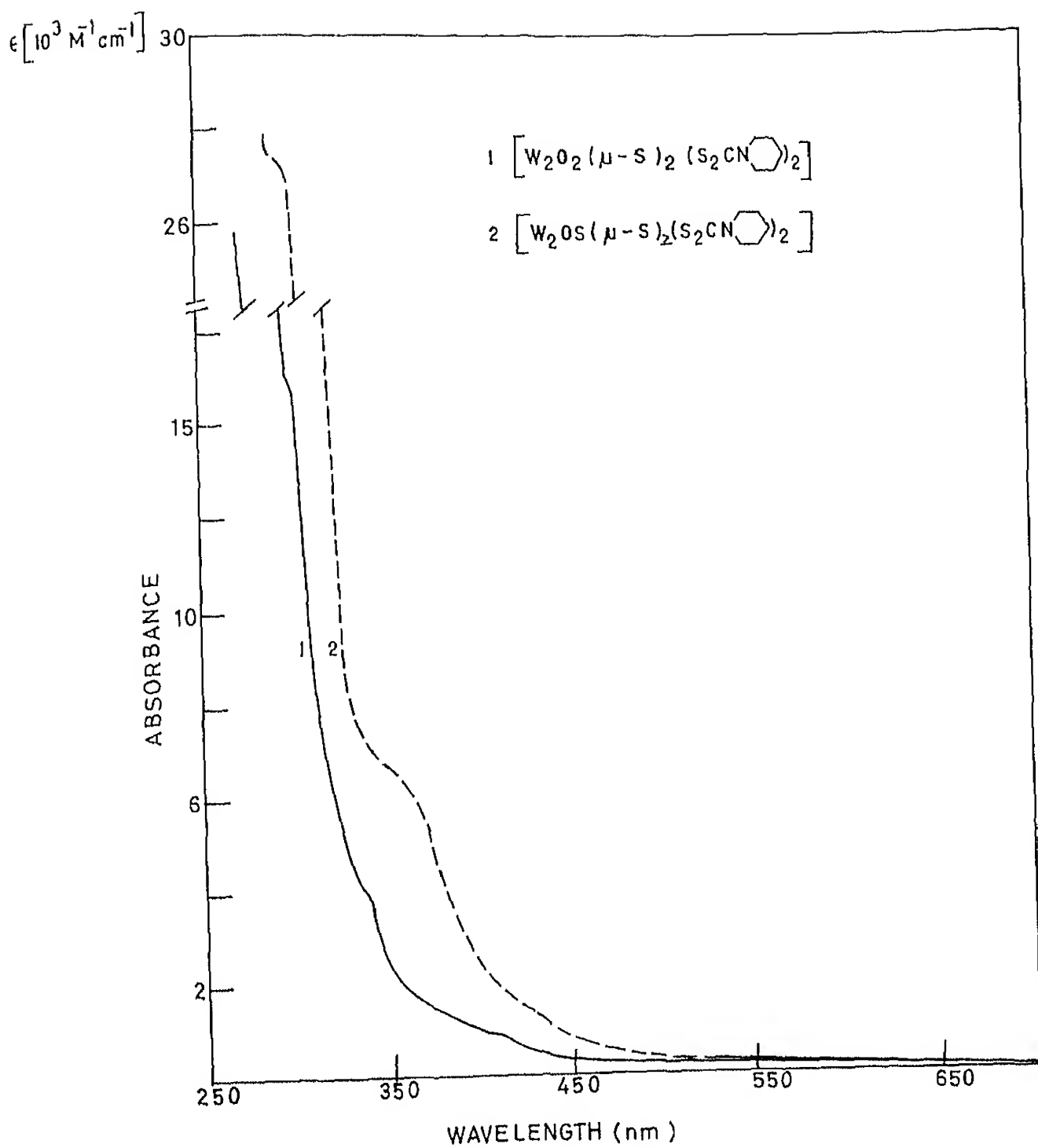
FIG 4.2.14   ELECTRONIC SPECTRA

been observed in similar dithiolene complexes.[148] The electronic

spectrum of $(Et_4N)_2[W(S_2C_2(COPh)_2)_3]$, reproduced in Fig. 4.2.7

shows only two absorptions in the visible region at 600 and

448 n.m. whereas the corresponding molybdenum complex $(Et_4N)_2$-

$[Mo(S_2C_2(COPh)_2)_3]$ shows three absorptions at 592, 412 and 336

n.m. in its electronic spectrum.[131] Stiefel and coworkers have also

synthesized similar tris-dithiolene complexes of W(IV) and Mo(IV)

with different substituents. They also experienced similar dis-

crepancy in these systems.[152]

The electronic spectrum of $K_4[W_2O_2(\mu-S)_2(CN)_6].3H_2O$ is

reproduced in Fig. 4.2.8. The electronic spectrum of this complex

has many absorptions in the u.v. region at 325, 268, 238 and 210 n.m.

which may be attributed to charge transfer transitions originating

from coordinated cyanide.[146] The absorption at 425 n.m. can be

assigned to charge transfer from bridged sulfido groups to tungs-

ten(V). It is important to note that in the complex, $[W_2O_2(\mu-S)_2$-

$(S_2CNEt_2)_2]$ an absorption appears at 415 n.m. Hence the absorp-

tion in the range 415-420 n.m. in sulfido bridged complexes,

studied here may be mainly originating from the bridged sulfido

groups to tungsten(V) charge transfer.

Electronic absorption spectra of trinuclear clusters

$[W^{IV}O(W^{VI}S_4)_2]^{2-}$ and $[W^{IV}S(W^{VI}S_4)_2]^{2-}$ are reproduced in Figs.

4.2.4 and 4.2.5 and data are presented in Table 4.6. All these

transitions are of charge transfer type and have been discussed

in detail by several groups.[40,86]

Table 4.5 Electronic Spectral Data

Complex	Solvent	λ_{max} (ε) (nm)	Reference
$(Me_4N)[Mo_2O_2(\mu-S)_2(S_2)_2]$	CH_3CN	463 (2.0×10^3) 377(sh) 305 (10.6×10^3) 278 (11.3×10^3)	86
$(Et_4N)_2[W_2O_2(\mu-S)_2(S_2)_2]$	CH_3CN	430 (2.3×10^3) 380(sh) 260 (41.3×10^3)	This work
$(Me_4N)_2[Mo_2O_2(\mu-S)_2(S_2)_2]$		440 (2.0×10^3) 400(sh) 280 (33.2×10^3)	This work
$K_4[W_2O_2(\mu-S)_2(CN)_6]$	H_2O	425 (0.15×10^3) 325 (1.4×10^3) 268 (5.1×10^3) 238 (5.5×10^3) 210 (6.3×10^3)	This work
$(Et_4N)_2[W_2O_2(\mu-S)_2(S_2C_2(COPh)_2)_2]$	DMF	382 (11.5×10^3) 316 (31.8×10^3)	This work
$(Et_4N)_2[W_2O_2(\mu-S)_2(S_2C_2(COOMe)_2)_2]$	DMF	460 (2.4×10^3) 345 (14×10^3)	This work
$(Et_4N)_2[Pd(S_2C_2(COPh)_2)_2]$	DMF	557 (6.1×10^3) 498(sh) 325 (46×10^3)	148
$(Et_4N)_2[W(S_2C_2(COPh)_2)_3]$	DMF	600 (1.9×10^3) 448 (11.6×10^3)	This work
$(Et_4N)_2[Mo(S_2C_2(COPh)_2)_3]$	DMF	592 (5.8×10^3) 412 (9.4×10^3) 336 (10.5×10^3)	133

Table 4.6   Electronic Spectral Data

Complex	Solvent	λ_{max} (nm)
$(Et_4N)_2[WS(WS_4)_2]$	CH_3CN	538(sh)
		390
$(Ph_4As)_2[WS(WS_4)_2]$	CH_3CN	540(sh)
		390
$(Et_4N)_2[WO(WS_4)_2]$	CH_3CN	440
		378
$(PhCH_2Et_3N)_2[WO(WS_4)_2]$	CH_3CN	440
		378
$(2\ Cl-C_2H_4Me_2NH)_2[WO(WS_4)_2]$	CH_3CN	440
		380

Table 4.7   Electronic Spectral Data

Complex	Solvent	λ_{max} (ϵ) (nm)	Reference
1	2	3	4
$[MoO(S_2)(S_2CNEt_2)_2]$	CH_3CN	578 (1.2×10^3) 391 (3.4×10^3)	63
$[WO(S_2)(S_2CNEt_2)_2]$	CH_2Cl_2	480 (1.8×10^3) 438 (2.4×10^3) 340(sh) 320 (9.3×10^3)	This work
$[WO(S_2)(S_2CNPr_2)_2]$	CH_2Cl_2	480 (1.8×10^3) 435 (2.6×10^3) 345(sh) 325 (9.2×10^3)	This work
$[WO(S_2)(S_2CN\langle \hexagon \rangle)_2]$	CH_2Cl_2	480 (1.9×10^3) 435 (2.7×10^3) 345(sh) 325 (9.4×10^3)	This work
$[WS(S_2)(S_2CNBu_2)_2]$	–	602 394 360	149
$[WS(S_2)(S_2CNEt_2)_2]$	CH_2Cl_2	600 (3.4×10^3) 390 (10.8×10^3) 360 (9.8×10^3)	This work
$[WS(S_2)(S_2CNPr_2)_2]$	CH_2Cl_2	600 (3.2×10^3) 390 (10.4×10^3) 356 (9.3×10^3)	This work

Table 4.7 (contd.)

1	2	3	4
$[WS(S_2)(S_2CN\bigcirc)_2]$	CH_2Cl_2	600 (2.8×10^3) 392 (8.6×10^3) 356 (7.4×10^3)	This work
$(Et_2NH_2)[WO(S_2)_2(S_2CNEt_2)]$	CH_2Cl_2	480 (0.8×10^3) 412 (1.3×10^3) 322 (4.4×10^3)	This work
$(Pr_2NH_2)[WO(S_2)_2(S_2CNPr_2)]$	CH_2Cl_2	475 (1.1×10^3) 408 (1.7×10^3) 325 (4.2×10^3)	This work
$[WO(S_2CNEt_2)_2]$	CH_2Cl_2	400(sh) 340 (2.3×10^3)	This work
$[WO(S_2CN\bigcirc)_2]$	CH_2Cl_2	400(sh) 340 (2.1×10^3)	This work

Table 4.8   Electronic Spectral Data

Complex	Solvent	λ_{max} (ε) (nm)
$[W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$	CH_2Cl_2	415 (0.2×10^3)
		332 (1.5×10^3)
		296 (7.6×10^3)
$[W_2O_2(\mu\text{-}S)_2(S_2CN\bigcirc)_2]$	CH_2Cl_2	410 (0.8×10^3)
		338 (3.8×10^3)
		300 (14.6×10^3)
$[W_2OS(\mu\text{-}S)_2(S_2CNEt_2)_2]$	CH_2Cl_2	418 (0.7×10^3)
		352 (4.4×10^3)
		295 (27.400)
$[W_2OS(\mu\text{-}S)_2(S_2CN\bigcirc)_2]$	CH_2Cl_2	422 (1.4×10^3)
		352 (6.6×10^3)
		297 (30.3×10^3)
$[W_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$	CH_2Cl_2	420 (2.2×10^3)
		382 (6.5×10^3)
		292 (30.1×10^3)

4.2.3 Magnetic Resonance Studies

^{1}H NMR Spectra

^{1}H NMR spectra of some of the complexes are reproduced in Figs. 4.3.1 to 4.3.4. Chemical shifts relative to TMS and assignments are presented in Table 4.9. The spectrum of (Et_2NH_2)-$[WO(S_2)_2(S_2CNEt_2)]$ shows besides methyl and methylene protons, two sets of methylene protons at 3.4 and 3.85 δ ppm. The splitting of these methylene protons arising from diethylaminium cation is not properly understood.

The complex $[WO(S_2)(S_2CNEt_2)_2]$ differs from $[WS(S_2)(S_2CNEt_2)_2]$ only in containing a more electronegative atom at terminal position. This difference is clearly reflected by the expected chemical shifts of the protons in the ^{1}H NMR spectra. The general feature of these spectra are very much identical to those reported for $[MoO(S_2)(S_2CNEt_2)_2]$.[63]

The ^{1}H NMR spectral data for $[W_2O_2(\mu-S)_2(S_2CNEt_2)_2]$, $[W_2OS(\mu-S)_2(S_2CNEt_2)_2]$ and $[W_2S_2(\mu-S)_2(S_2CNEt_2)_2]$ show that the replacement of oxygen by sulfur causes downfield shift of both methyl as well as methylene protons. A similar trend has been observed in analogous molybdenum complexes.[97] An interesting difference between the spectrum of $[Mo_2OS(\mu-S)_2(S_2CNEt_2)_2]$ and its tungsten analog, $[W_2OS(\mu-S)_2(S_2CNEt_2)_2]$ is that the former complex gives doublet of the triplet whereas the tungsten analog shows doublet of the quartet.[97]

$(Et_2NH_2)\left[WO(S_2)_2(S_2CNEt_2)\right]$

PPM (δ)

FIG. 4.3.1 ^1H NMR SPECTRUM
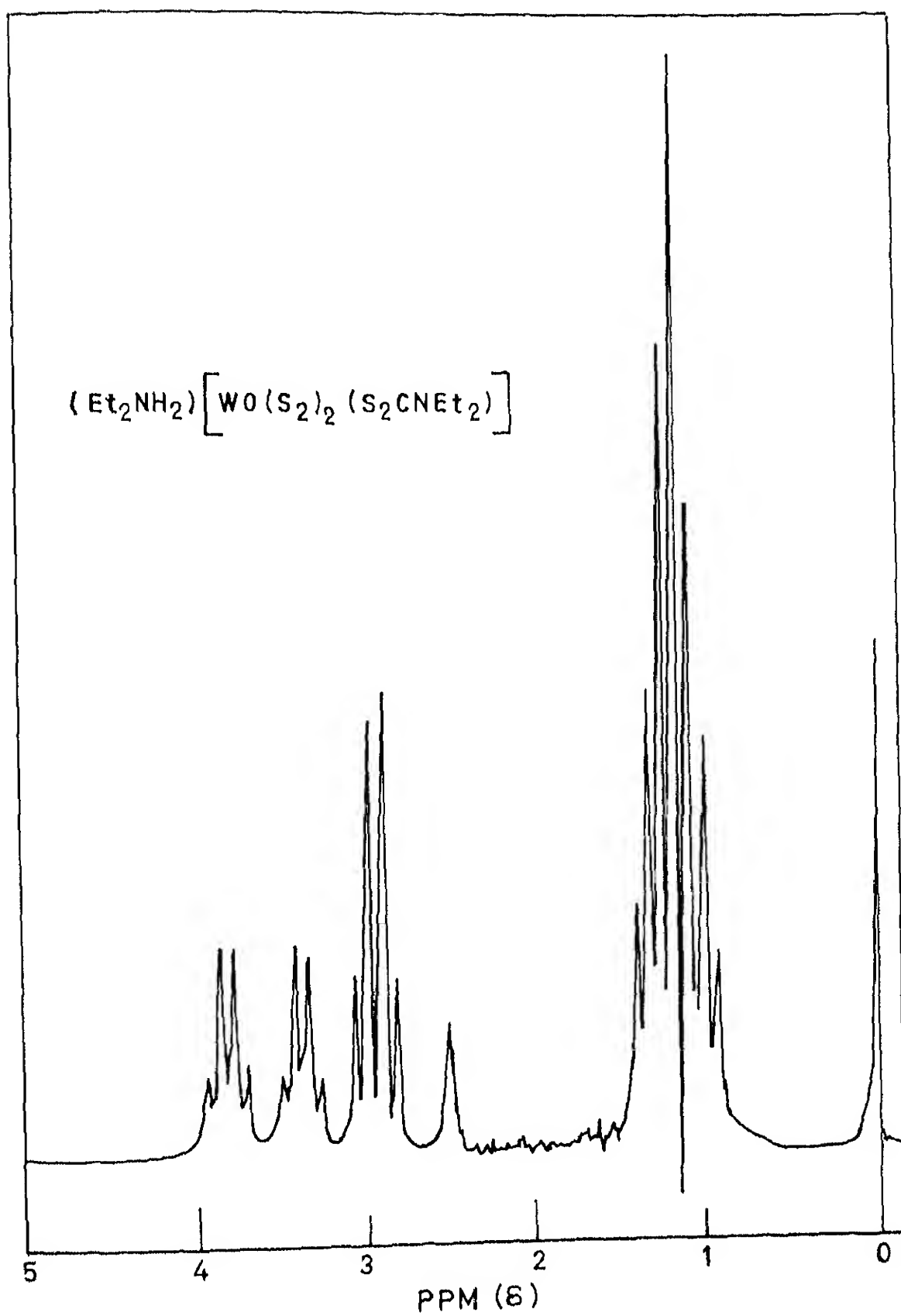
$[WO(S_2)(S_2CNEt_2)_2]$
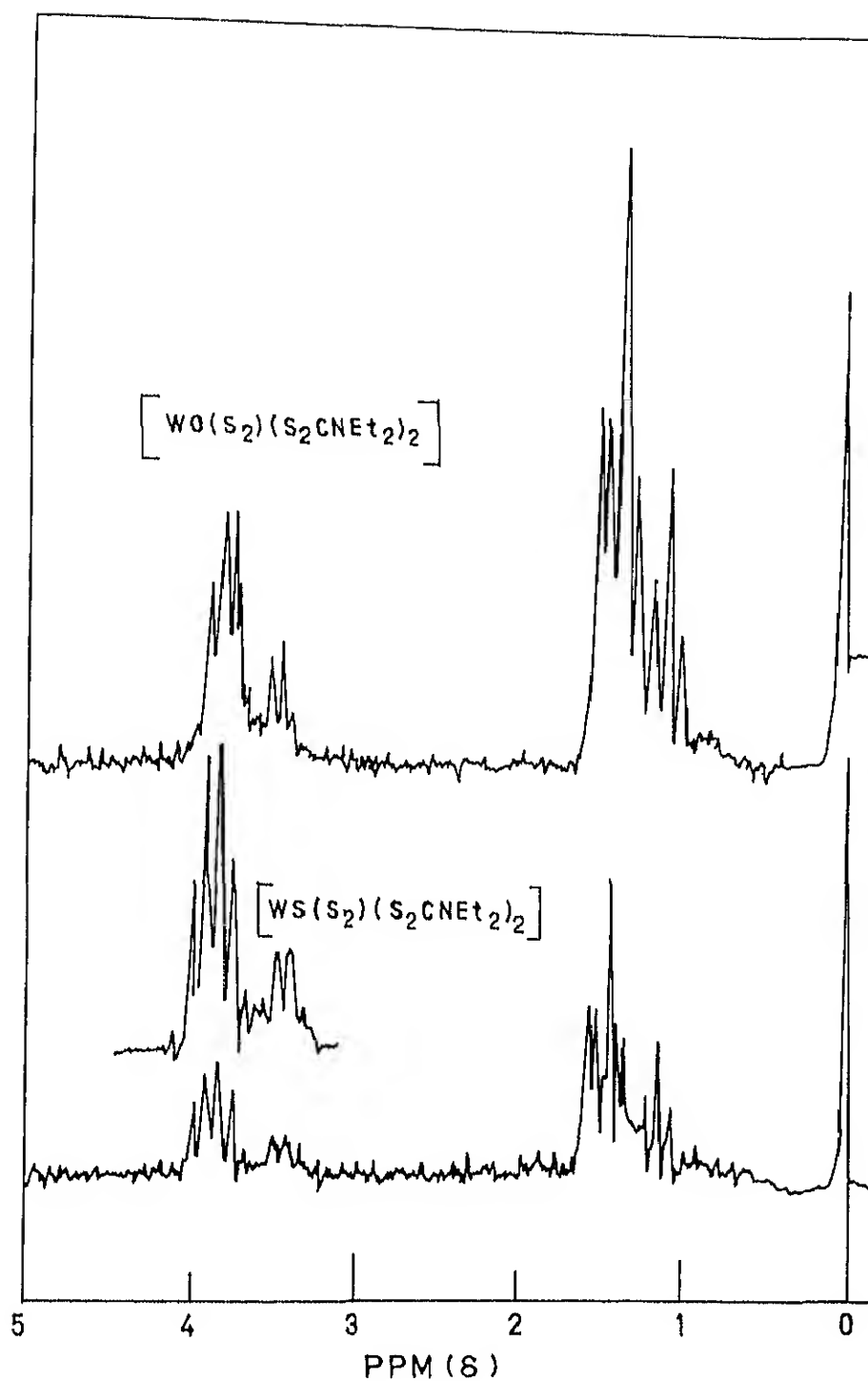
$[WS(S_2)(S_2CNEt_2)_2]$

FIG 4.3.2 ^1H NMR SPECTRA
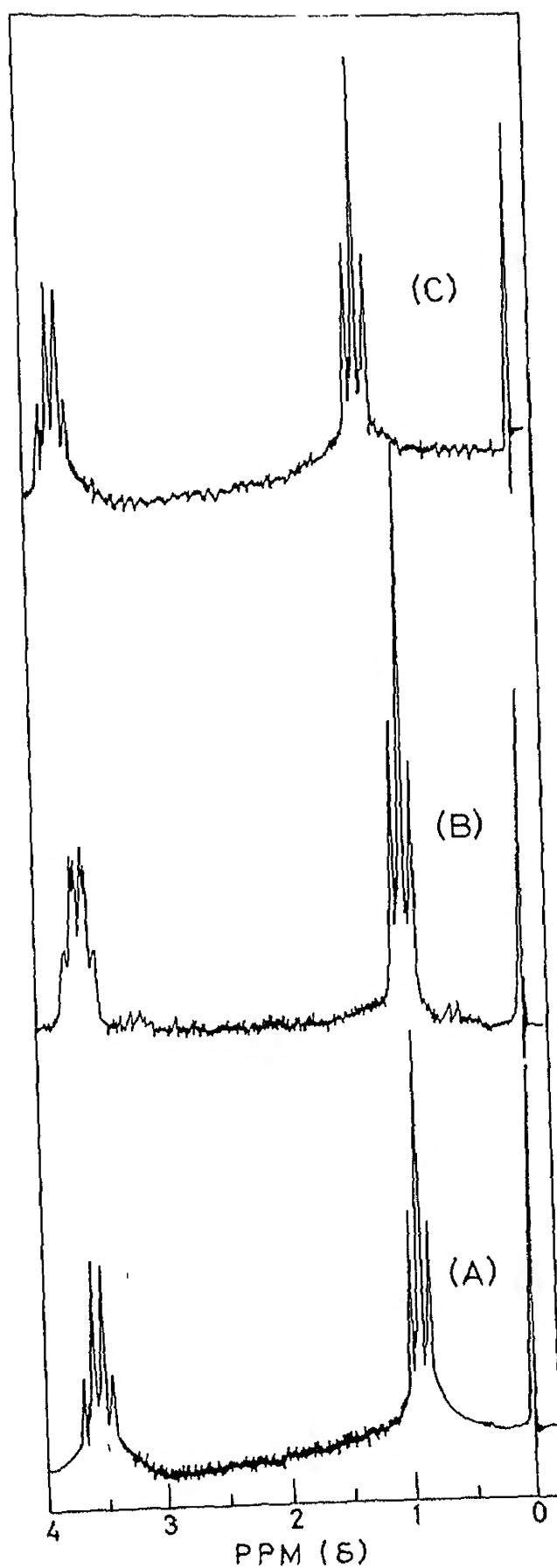
FIG. 4.3.3 ^{1}H NMR SPECTRA: (A) $[W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$;
(B) $[W_2OS(\mu\text{-}S)_2(S_2CNEt_2)_2]$ and (C) $[W_2S_2\text{-}$
$(\mu\text{-}S)_2(S_2CNEt_2)_2]$ in C_5D_5N.

$(Et_4N)_2[W_2O_2(\mu\text{-}S)_2(S_2C_2(COOMe)_2)_2]$

$(Et_4N)_2[W_2O_2(\mu\text{-}S)_2(S_2C_2(COph)_2)_2]$
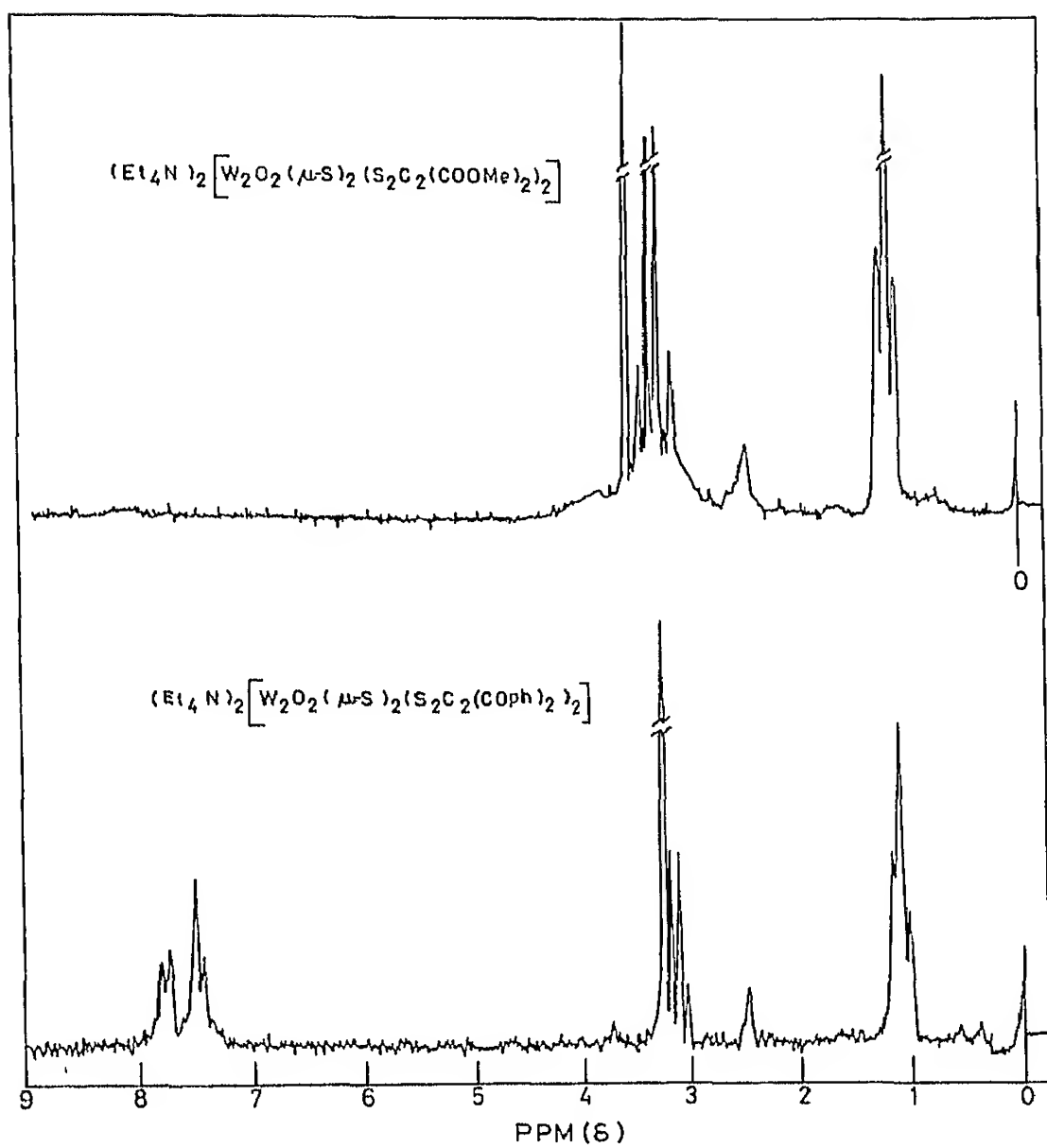
FIG 4 3 4 ^{1}H NMR SPECTRA

Table 4.9 ^{1}H NMR Spectral Data

Complex	Solvent	Absorption δ(ppm)
1	2	3
$(Et_2NH_2)[WO(S_2)_2(S_2CNEt_2)]$	DMSO-d_6	0.9-1.5 (tt, CH_3, 12H)
		2.95 (q, CH_2, 4H)
		3.4 (q, CH_2, 2H)
		3.85 (q, CH_2, 2H)
$[MoO(S_2)(S_2CNEt_2)_2]$	$CDCl_3$	1.41 (t)[36]
		1.45 (t)
		3.97 (q)
		4.02 (q)
$[WO(S_2)(S_2CNEt_2)_2]$	$CDCl_3$	1.1 (t, CH_3, 3H)
		1.21-1.61 (m, CH_3, 9H)
		3.48 (q, CH_2, 4H)
		3.61-4.0 (q, CH_2, 4H)
$[WS(S_2)(S_2CNEt_2)_2]$	$CDCl_3$	1.18 (t, CH_3, 3H)
		1.26-1.68 (m, CH, 9H)
		3.48 (q, CH_2, 4H)
		3.7-4.05 (q, CH_2, 4H)
$[WO(S_2)(S_2CNPr_2)_2)$	$CDCl_3$	0.66-1.15 (m, CH_3, 6H)
		1.5-2.1 (m, CH_3, 6H)
		3.41 (q, CH_2, 4H)
		3.73 (q, CH_2, 12H)

Table 4.9 (contd.)

1	2	3
$[WS(S_2)(S_2CNPr_2)_2]$	$CDCl_3$	0.66-1.2 (m, CH_3, 6H)
		1.5-2.1 (m, CH_3, 6H)
		3.3 (q, CH_2, 4H)
		3.72 (q, CH_2, 12H)
$[W_2O_2(\mu\text{-S})_2(S_2CNEt_2)_2]$	C_5D_5N	0.95 (t, CH_3, 12H)
		3.54 (q, CH_2, 8H)
$[W_2OS(\mu\text{-S})_2(S_2CNEt_2)_2]$	C_5D_5N	0.98 (t, CH_3, 12H)
		3.62 (q, CH_2, 8H)
$[W_2S_2(\mu\text{-S})_2(S_2CNEt_2)_2]$	C_5D_5N	1.08 (t, CH_3, 12H)
		3.74 (q, CH_2, 8H)
$(Et_4N)_2[Mo_2O_2(\mu\text{-S})_2(S_2C_2(COOMe)_2)_2]$	DMSO-d_6	1.11 (t, cation CH_3, 24H)[78]
		3.13 (q, cation CH_2, 16H)
		3.72 (s, ester, 6H)
		3.77 (s, ester, 6H)
$(Et_4N)_2[W_2O_2(\mu\text{-S})_2(S_2C_2(COOMe)_2)_2]$	DMSO-d_6	1.14 (t, cation, CH_3, 24H)
		3.28 (q, cation CH_2, 16H)
		3.5 (s, ester, 12H)
$(Et_4N)_2[W_2O_2(\mu\text{-S})_2(S_2C_2(COPh)_2)_2]$	DMSO-d_6	1.1 (t, cation CH_3, 24H)
		3.2 (q, cation CH_2, 16H)
		7.2-8.0 (m, O-Ph, 20 H)
$(Et_4N)_2[W(S_2C_2(COPh)_2)_3]$	DMSO-d_6	1.16 (t, cation CH_3, 24H)
		3.23 (q, cation CH_2, 16H)
		7.2-8.0 (m, O-Ph, 30H)

s = singlet, t = triplet, q = quartet, m = multiplet.

^{1}H NMR spectroscopy was found to be very helpful in under-standing the mode of insertion of acetylene in $(Et_4N)_2[W_2O_2(\mu-S)_2-(S_2)_2]$. In the case of its molybdenum analog, the insertion was found to take place across Mo-S bond, as two singlets at 3.72 and 3.77
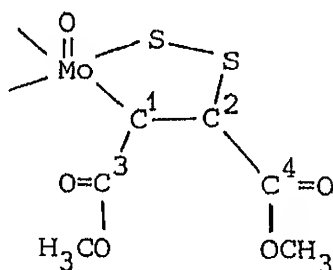
for -OCH$_3$ attached to two different carbon atoms, C-3 and C-4 were observed. However, ^{1}H NMR spectrum of $(Et_4N)_2[W_2O_2(\mu-S)_2-(S_2C_2(COOMe)_2)_2]$ shows only a singlet in this region, suggesting the identical nature of two methoxy groups in the resulting complex. On the basis of the above observations, it has been suggested that the insertion takes place across S-S bond and dithiolene ligated complex is formed. Further support to this proposition comes from ^{13}C NMR studies (vide infra).

^{13}C NMR Spectra

^{13}C NMR studies were carried out to understand the nature of insertion reaction of the activated acetylene, DBA, with {W<S| S} moiety. There are reports that the insertion may take place across Mo-S or S-S bond in molybdenum-sulfur complexes with the formation of vinyl disulfide or dithiolene coordinated complexes.[76-78]

$[(Et_4N)_2[W_2O_2(\mu-s)_2(S_2C_2(COph)_2)_2]$
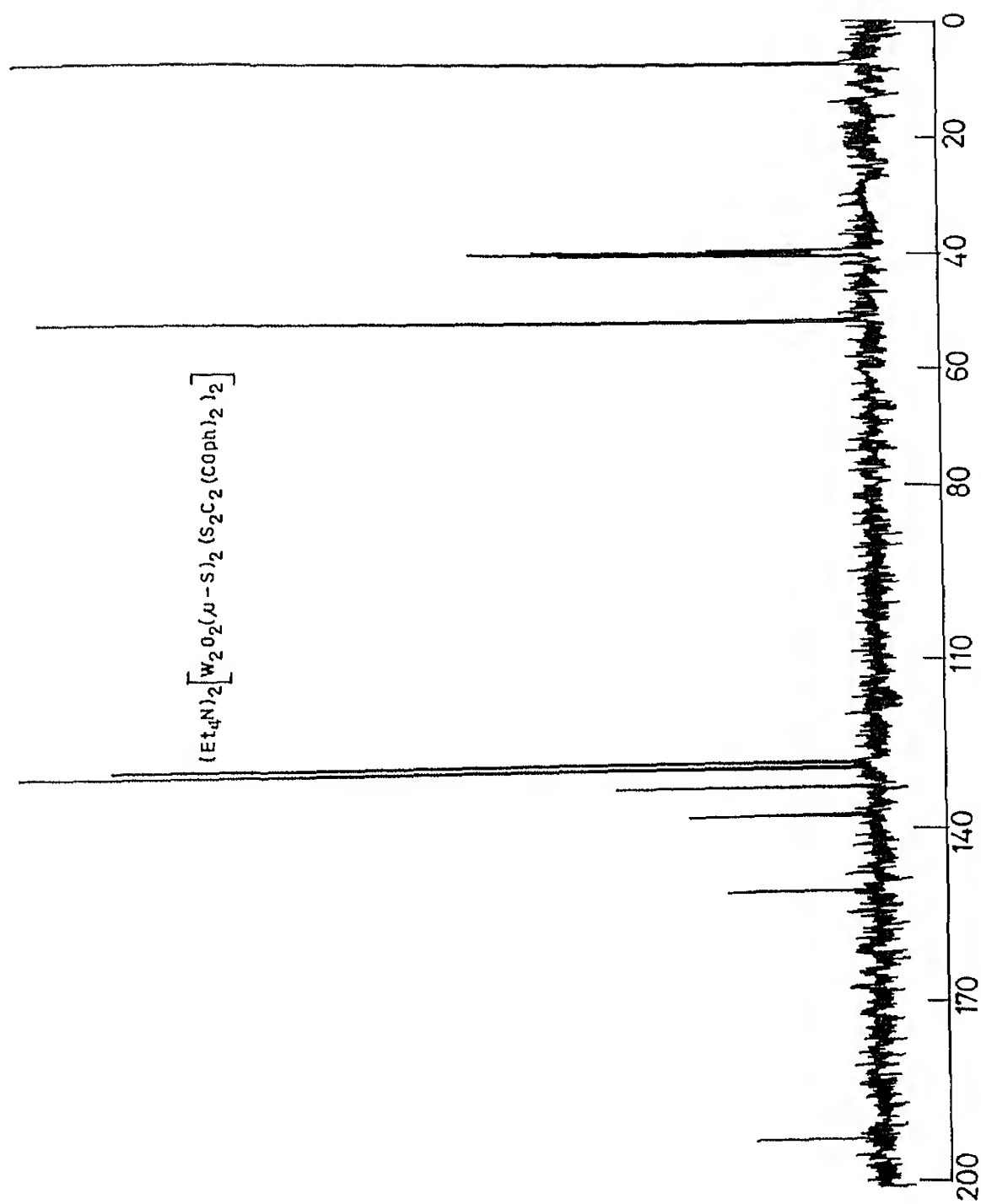
FIG 435 $^{13}CNMR$ SPECTRUM
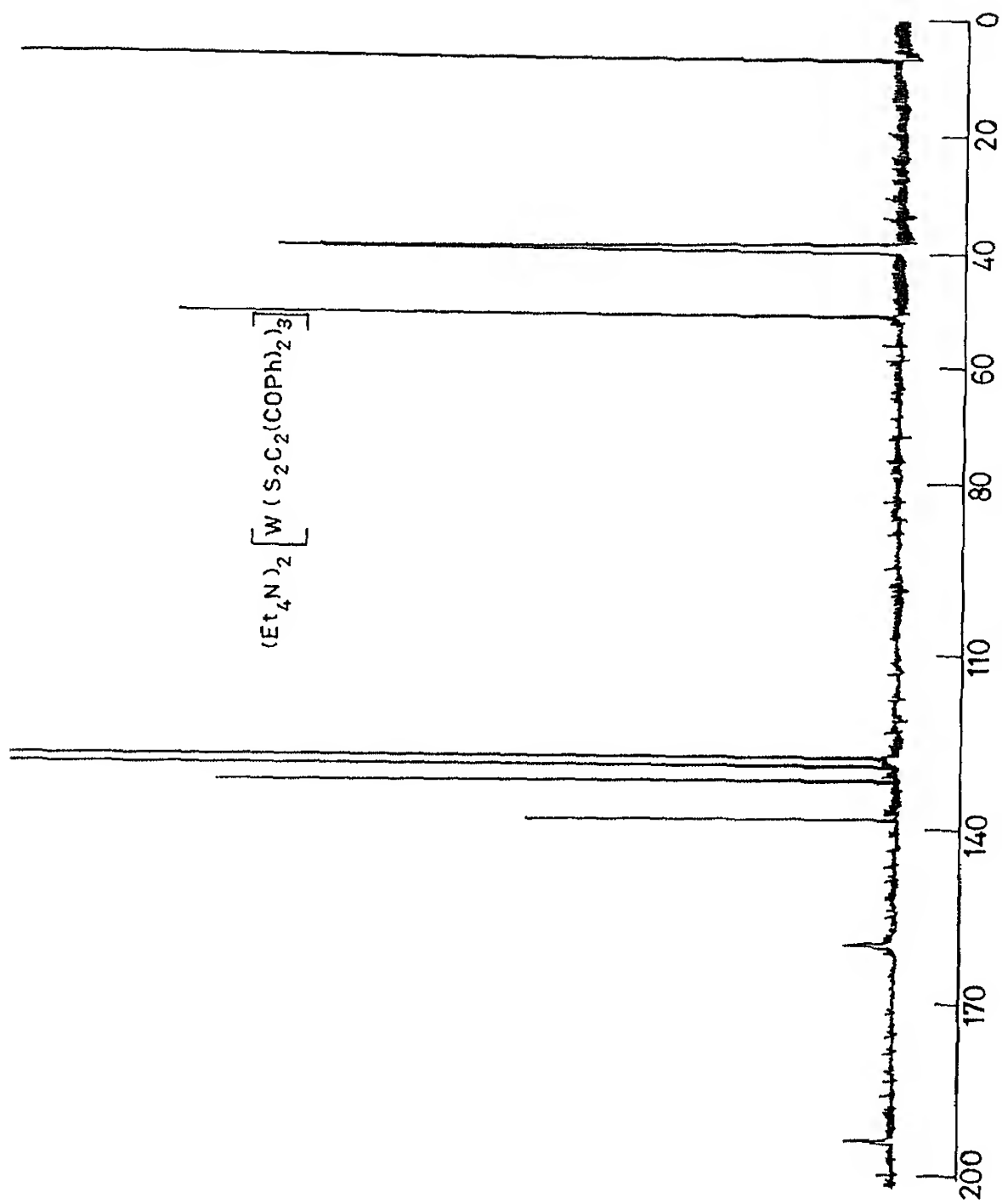
$(Et_4N)_2 \left[W(S_2C_2(COPh)_2)_3 \right]$

FIG 4 3 6 ^{13}C NMR SPECTRUM

Table 4.10 ^{13}C NMR Chemical Shifts

Complex	Cation (CH$_2$, CH$_3$)	DMSO	Ph	C=C	CO	Reference
(Et$_4$N)$_2$[MoO(S$_2$C$_2$(COPh)$_2$)$_2$]	6.96 51.41	38.84– 40.63	137.56 132.11 129.02 127.85	148.53	193.92	137
(Et$_4$N)$_2$[W(S$_2$C$_2$(COPh)$_2$)$_3$]	6.96 51.41	38.86– 40.11	138.45 131.56 128.93 127.50	159.89	193.91	This work
(Et$_4$N)$_2$[W$_2$O$_2$(μ-S)$_2$(S$_2$C$_2$(COPh)$_2$)$_2$]	6.97 51.43	39.08– 39.91	137.45 132.35 129.02 127.97	150.44	193.93	This work

The complex $(Et_4N)_2[W_2O_2(\mu-S)_2(S_2C_2(COPh)_2)_2]$ shows ^{13}C NMR spectrum whichis very much similar to the spectra recorded for $(Et_4N)_2[MoO(S_2C_2(COPh)_2)_2]$[137] and $(Et_4N)_2[W(S_2C_2(COPh)_2)_3]$. These spectra are reproduced in Figs. 4.3.5 and 4.3.6 and chemical shifts relative to TMS are tabulated in Table 4.10. By analogy with other bis- and tris-dithiolene complexes of molybdenum and tungsten, prepared by insertion reactions ^{13}C NMR data can be interpreted. The ^{13}C NMR spectral data of $(Et_4N)_2[W_2O_2(\mu-S)_2-(S_2C_2(COPh)_2)_2]$ and $(Et_4N)_2[W(S_2C_2(COPh)_2)_3]$ are almost identical, suggesting the presence of similar ligands in both the cases. This indicates clearly that the mode of insertion in $[W_2O_2(\mu-S)_2-(S_2)_2]^{2-}$ is across S-S bond of $\{W\overset{S}{\underset{S}{\big|}}\}$ moiety, contrary to the molybdenum analog.[68]

ESR Spectra

All the complexes described in this dissertation are dia-magnetic and ESR inactive. However, during the formation of $[WO(S_2)(S_2CNEt_2)_2]$ and $[WS(S_2)(S_2CNEt_2)_2]$, ESR active species could be identified. The ESR spectra recorded during the forma-tion of these complexes are reproduced in Figs. 4.3.7 and 4.3.8. Hyperfine splitting due to ^{183}W (I = 1/2) is not readily detected though the natural abundance of this isotope is 14.28 %.[153] This is probably because of the high $\langle g \rangle$ value for this type of systems. The species under investigation give ESR signal which shows superhyperfine splitting suggesting the presence of two protons in the vicinity of the W(V) center. ESR studies have been
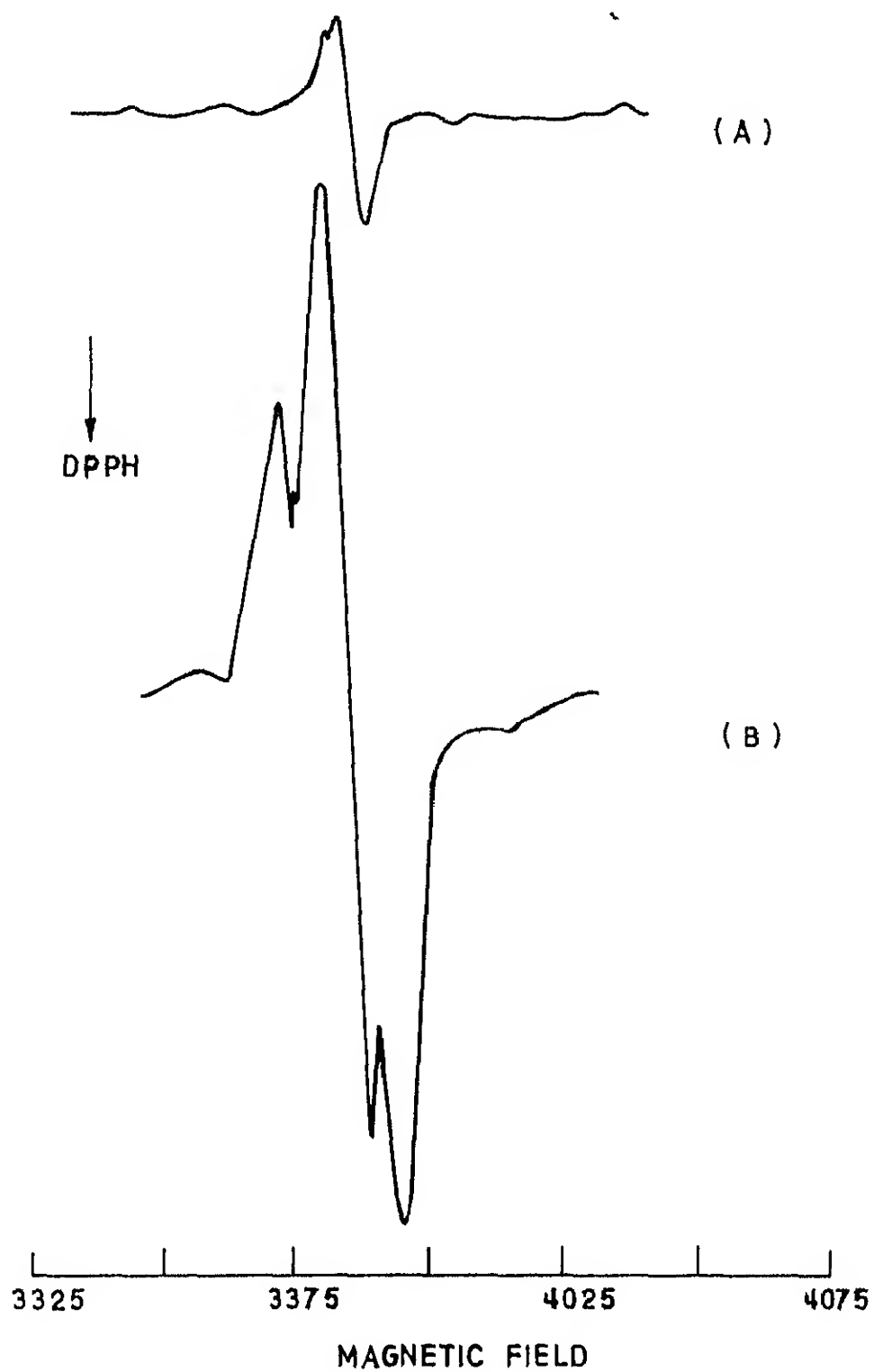
FIG. 4.3.7 ESR SPECTRA
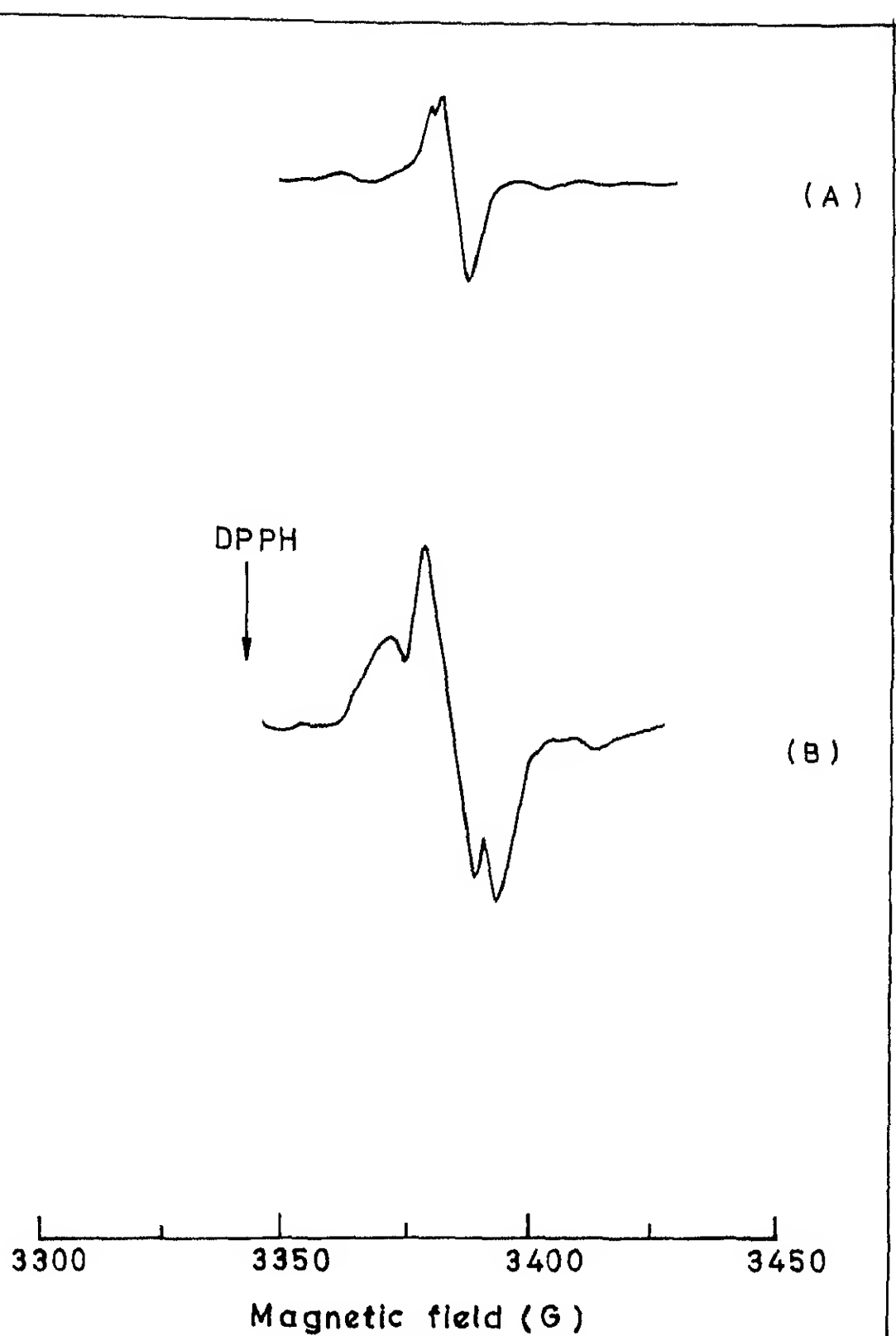
FIG.4.3.8 ESR SPECTRA

found to be very helpful in determining the path of the reaction.
When CS_2 is added to a DMF solution of $(Et_2NH_2)_2WOS_3$ or
$(Et_2NH_2)_2WS_4$ at room temperature in air, the ESR signal starts
appearing within 5 min which gains maximum intensity after 8 hr
and then starts decaying and ultimately disappears after 20 hr.
The super-hyperfine interaction with two protons is seen in the
ESR spectrum suggesting the presence of an intermediate species
containing $\{W^V(SH)_2\}$ moiety. A noteworthy feature of these spectra
is that the $\langle g \rangle$ values remain constant throughout, clearly indicat-
ing the involvement of only one W(V) species in this reaction.
On the basis of the above observations and the identification of the
superoxide ion radical during the course of the reaction, a pro-
bable mechanism has been suggested (vide supra, Eqn. 4.1).

4.2.4 C.V. Studies

Some of the complexes synthesized in the present study are
the products of induced electron transfer reactions. Thus, it is
important to study the electrochemical behaviour of some of these
complexes. The cyclic voltammetric (C.V.) study of these complexes
were carried out in CH_3CN and cyclic voltammograms are reproduced
in Figs. 4.5.1 to 4.5.3. The relevant data are given in Table 4.11.
The complex $(Et_2NH_2)[WO(S_2)_2(S_2CNEt_2)]$ which is presumed to be
formed by a series of electron transfer reactions (vide infra),
shows an irreversible redox behaviour. The low oxidation poten-
tial value is suggestive of facile redox capability of the attach-
ed ligand, persulfide or dithiocarbamate on oxidation. The
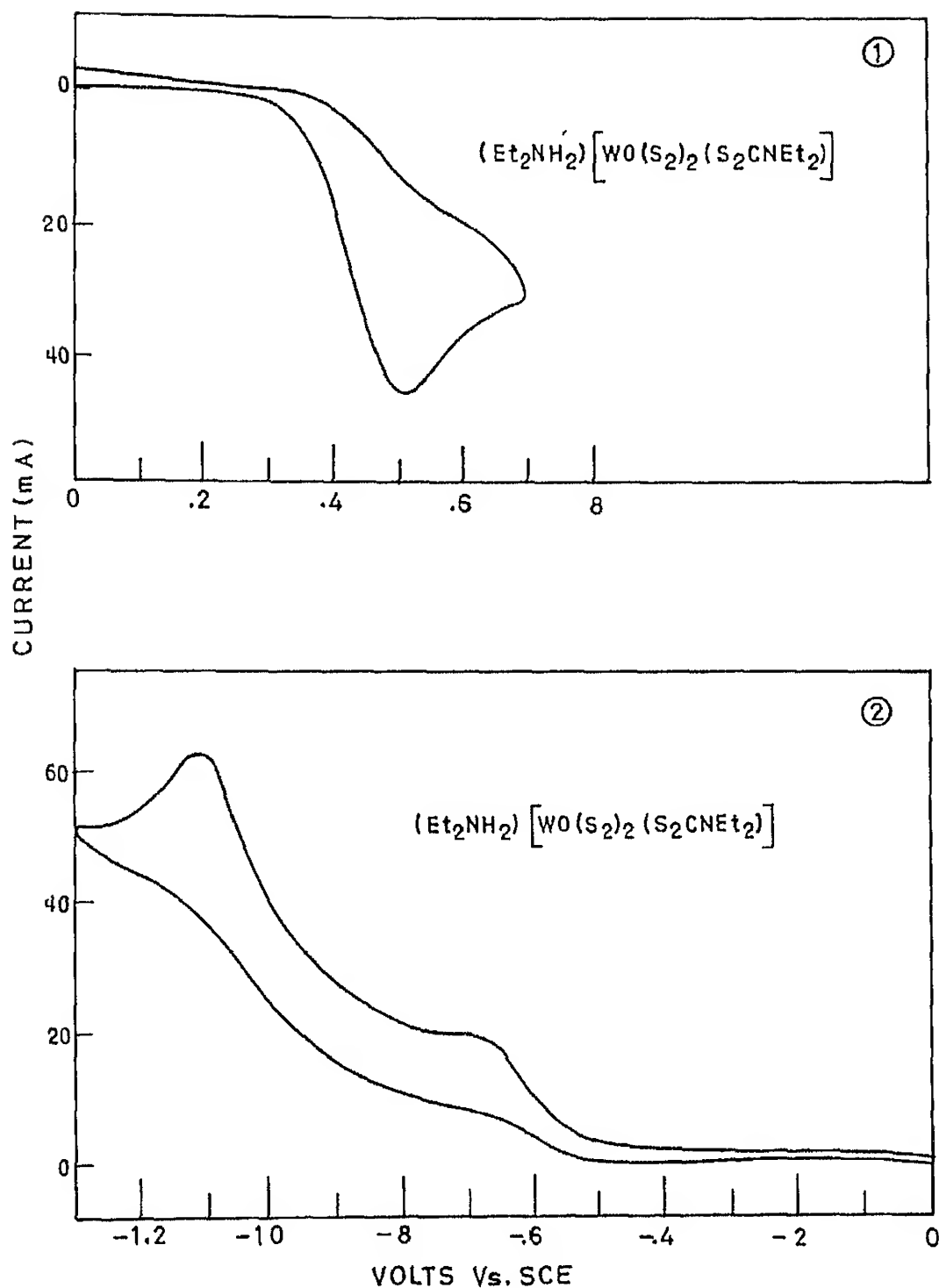
FIG. 4.41   CYCLIC VOLTAMMOGRAM 1. OXIDATION 2. REDUCTION
              SCAN RATE 50 mV s^{-1}
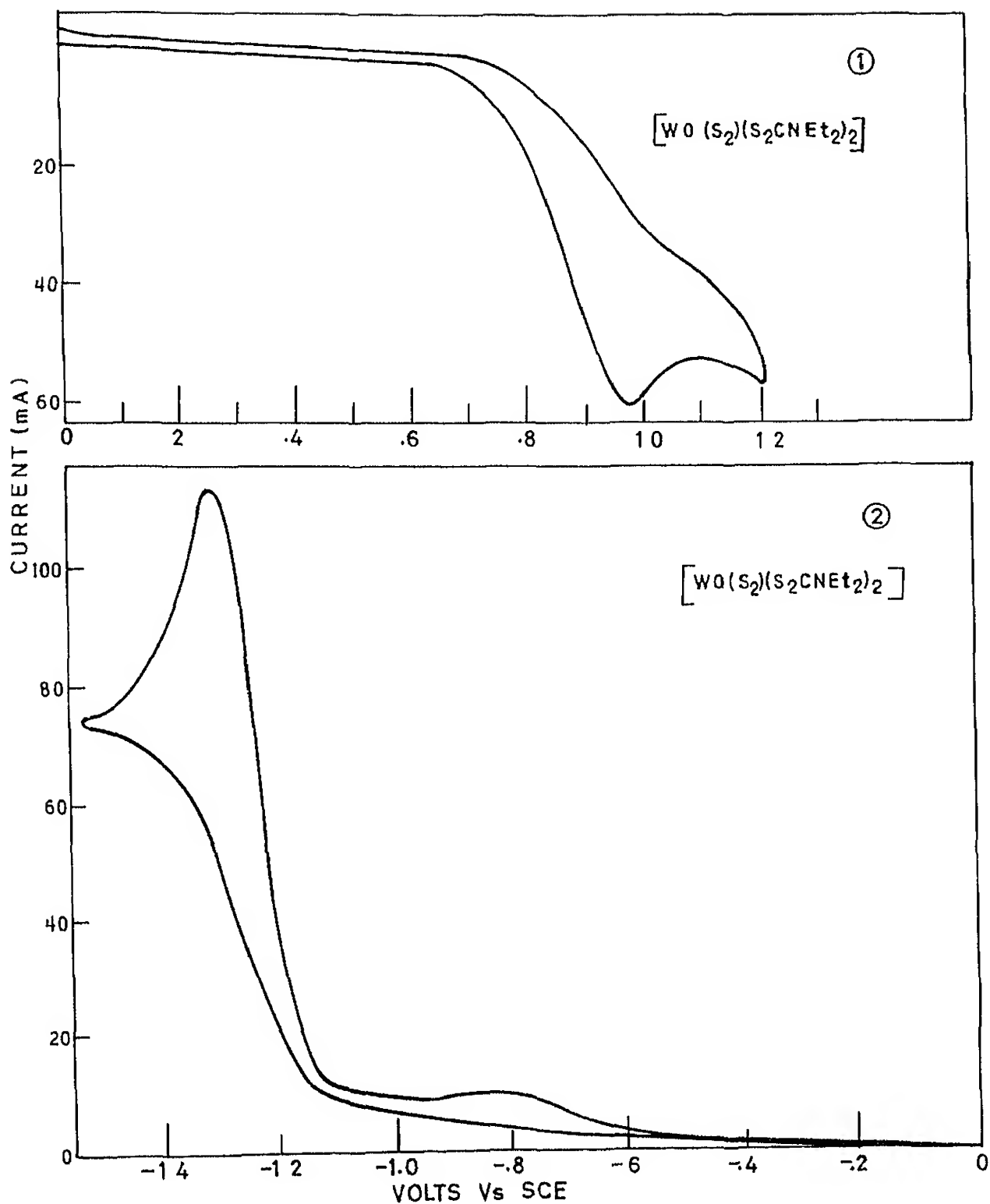
FIG 4.4.2   CYCLIC VOLTAMMOGRAM . 1 OXIDATION 2 REDUCTION
SCAN RATE 50 mVs⁻¹
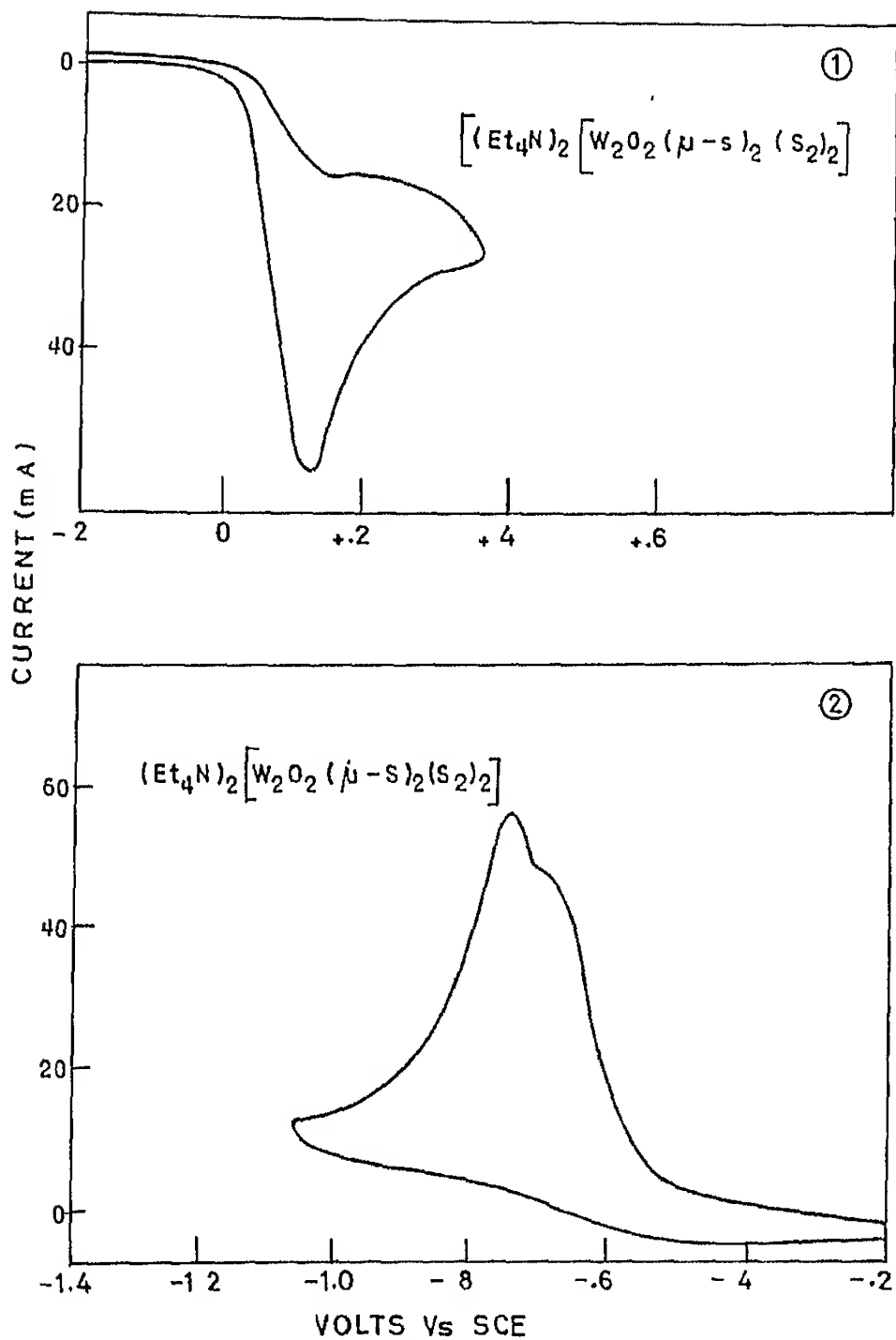
FIG. 4 4.3   CYCLIC VOLTAMMOGRAM . 1. OXIDATION 2. REDUCTION
            SCAN RATE 50 mV s⁻¹

Table 4.11 Electrochemical Redox Potentials[*] vs SCE

Complex	Concentration (CH$_3$CN)	Scan rate mVs^{-1}	Oxidation		Reduction	
			Potential (V)	Current (mV)	Potential (V)	Current (mA)
(Et$_2$NH$_2$)$_2$[WO(S$_2$)$_2$(S$_2$CNEt$_2$)]	1.5x10^{-3}	50	+0.50	47	-0.54 / -1.00	26 / 70
[WO(S$_2$)(S$_2$CNEt$_2$)$_2$]	1.05x10^{-3}	50	+0.98	60	-0.80 / -1.31	10 / 114
(Et$_4$N)$_2$[W$_2$O$_2$(μ-S)$_2$(S$_2$)$_2$]	1.19x10^{-3}	50	+0.12	58	-0.72	60

*0.1 M (Et$_4$N)ClO$_4$ was used as supporting electrolyte.

reduction potential value suggests the capability of the metal center and/or persulfide ligand to undergo reduction. The irreversible nature of these C.V. studies proved that the intermediate species preceded by this compound is entirely different.

A comparison of the cyclic voltammogram of (Et_2NH_2)-$[WO(S_2)_2(S_2CNEt_2)]$ and $[WO(S_2)(S_2CNEt_2)_2]$ suggests that the redox stability increases with the substitution of $(S_2)^{2-}$ by $(S_2CNEt_2)^-$ in such systems. For $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ the low oxidation potential values suggest the instability of this compound in oxidizing environment. We have also observed that the solution of this compound under aerial exposure gets oxidized slowly.

4.2.5 X-Ray Studies

X-Ray Photoelectron Spectra (XPS)

X-ray photoelectron spectroscopy can help to measure the core electron energies of elements in these complexes. This technique can also help to estimate the charge distribution on the various atoms of the complex. Some representative examples of the complexes described here, were subjected to this study and the spectra are reproduced in Figs. 4.5.1 to 4.5.6. The binding energies of tungsten and sulfur are tabulated in Table 4.12. For a comparative study XPS data of elemental sulfur, $[Mo_2O_2(\mu-S)_2(S_2)_2]^{2-}$, WO_4^{2-}, WS_4^{2-} and metallic tungsten are also incorporated in this table. The S(2p) binding energies in these

$(Et_4N)_2\left[W_2O_2(\mu-S)_2(S_2)_2\right]$

BINDING ENERGY (eV)

FIG. 4.5.1

INTENSITY

FIG 4.5.2

$(Et_4N)_2\left[W_2O_2(\mu-S)_2(S_2C_2(COPh)_2)_2\right]$

BINDING ENERGY (eV)

INTENSITY

$$\left[W_2O_2(\mu-S)_2(S_2CNEt_2)_2 \right]$$

INTENSITY

BINDING ENERGY (eV)

FIG 4.5.3

$\left[W_2 S_2 (\mu - S)_2 (S_2 C NEt_2) \right]$

INTENSITY

BINDING ENERGY (eV)

FIG 4.5.4

$[WS(S_2)(S_2CNEt_2)_2]$

FIG 4.5.5

BINDING ENERGY (eV)

INTENSITY

$(Et_2NH_2) \left[W O (S_2)_2 (S_2CNEt_2) \right]$

INTENSITY

BINDING ENERGY (eV)
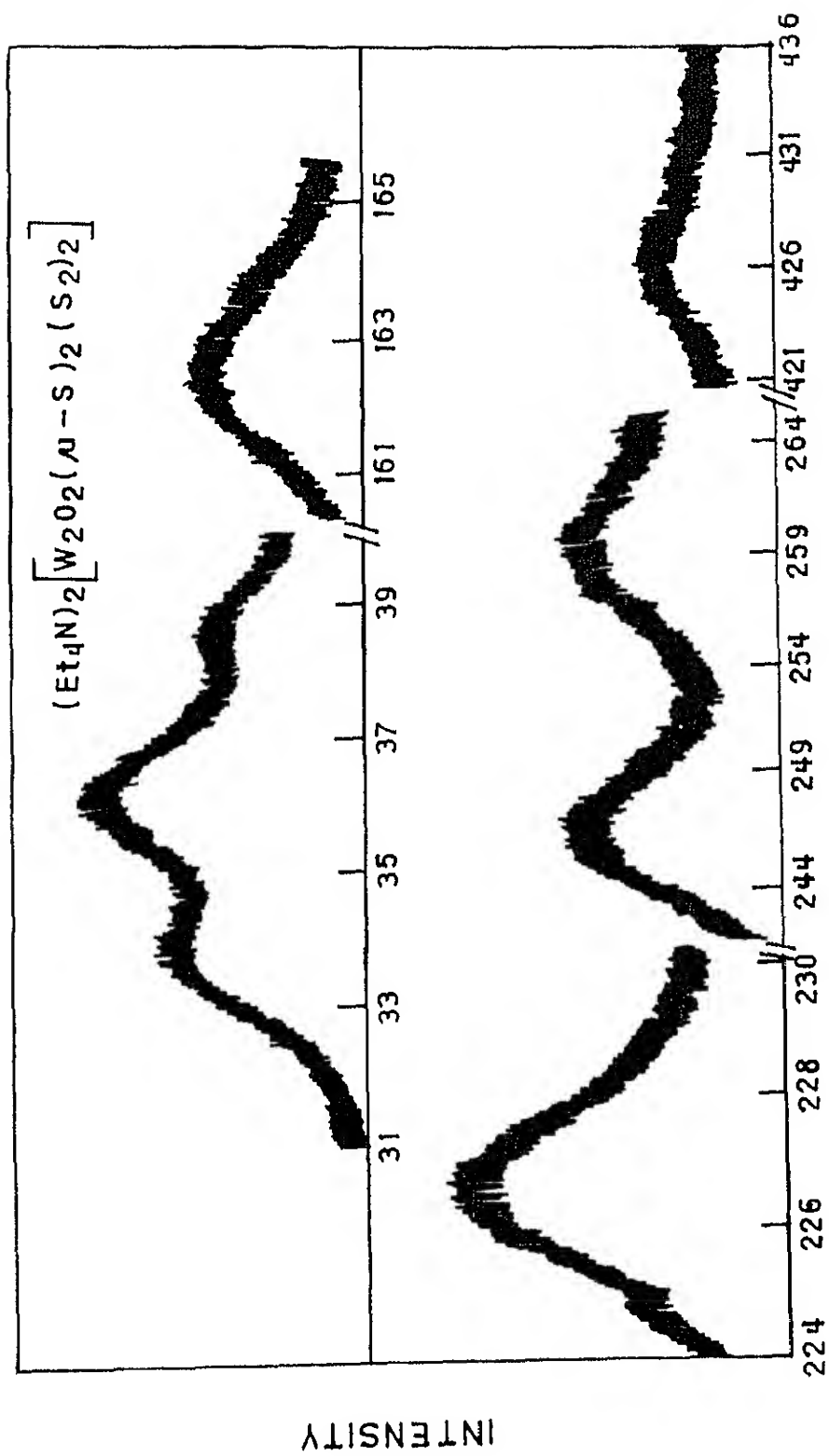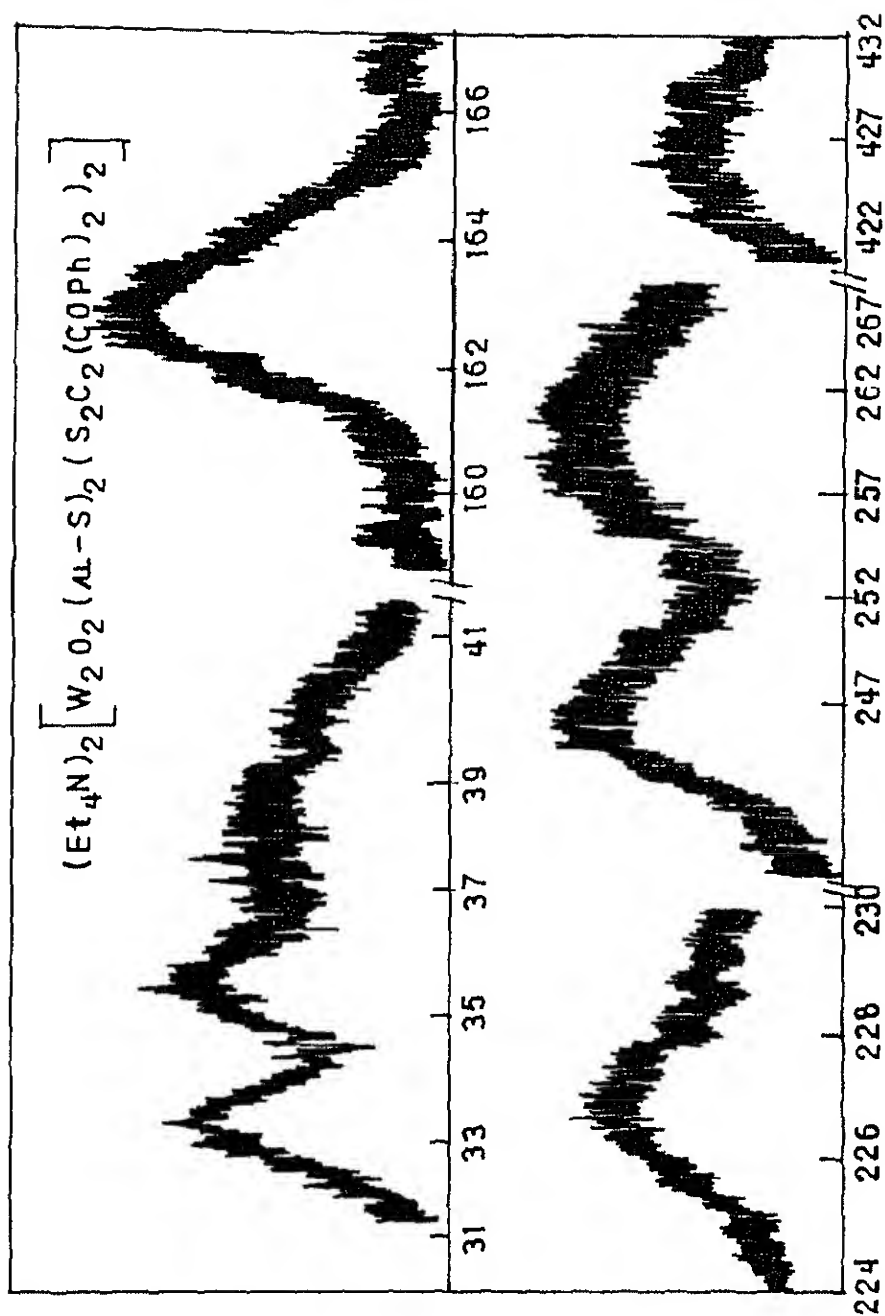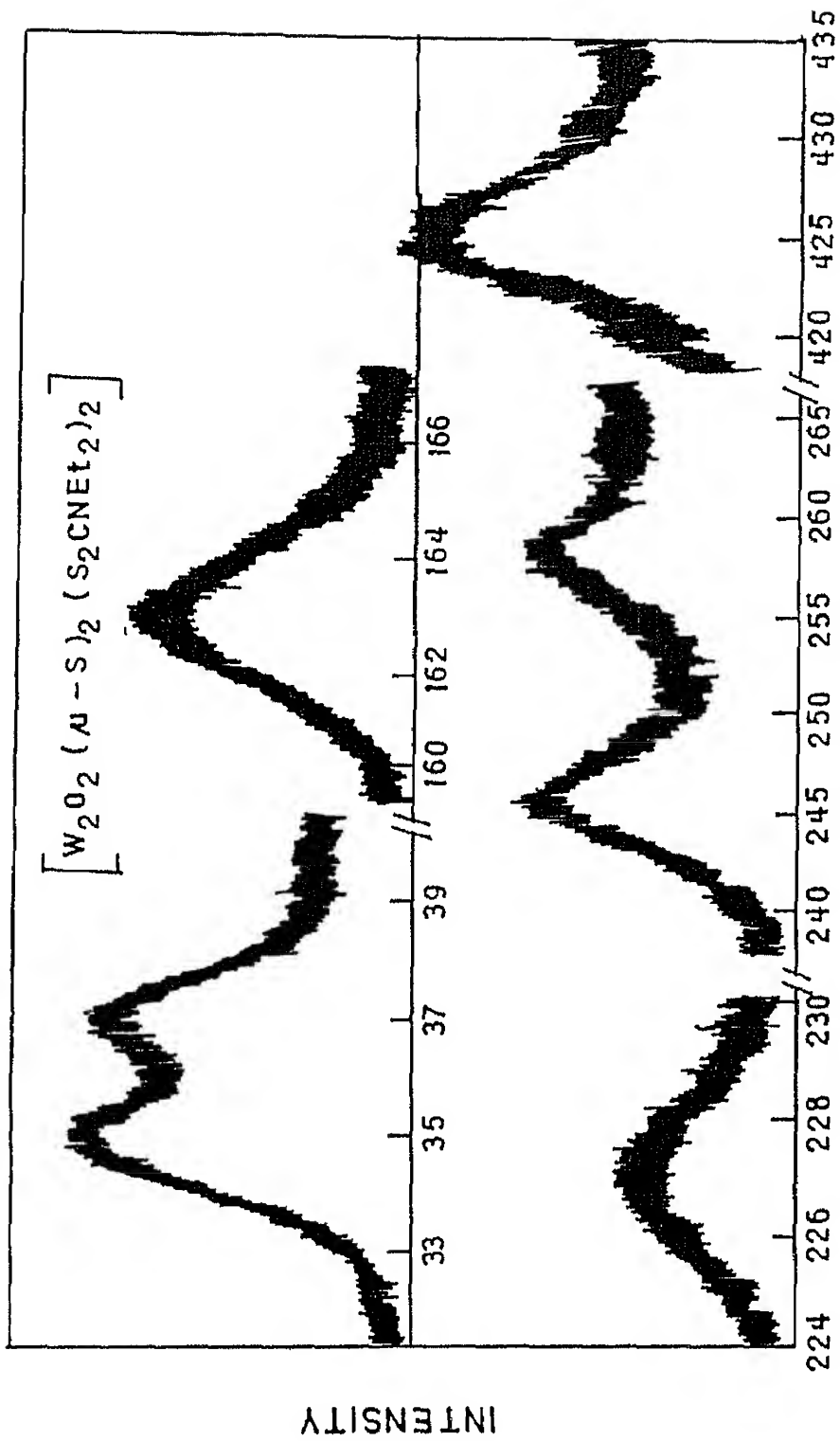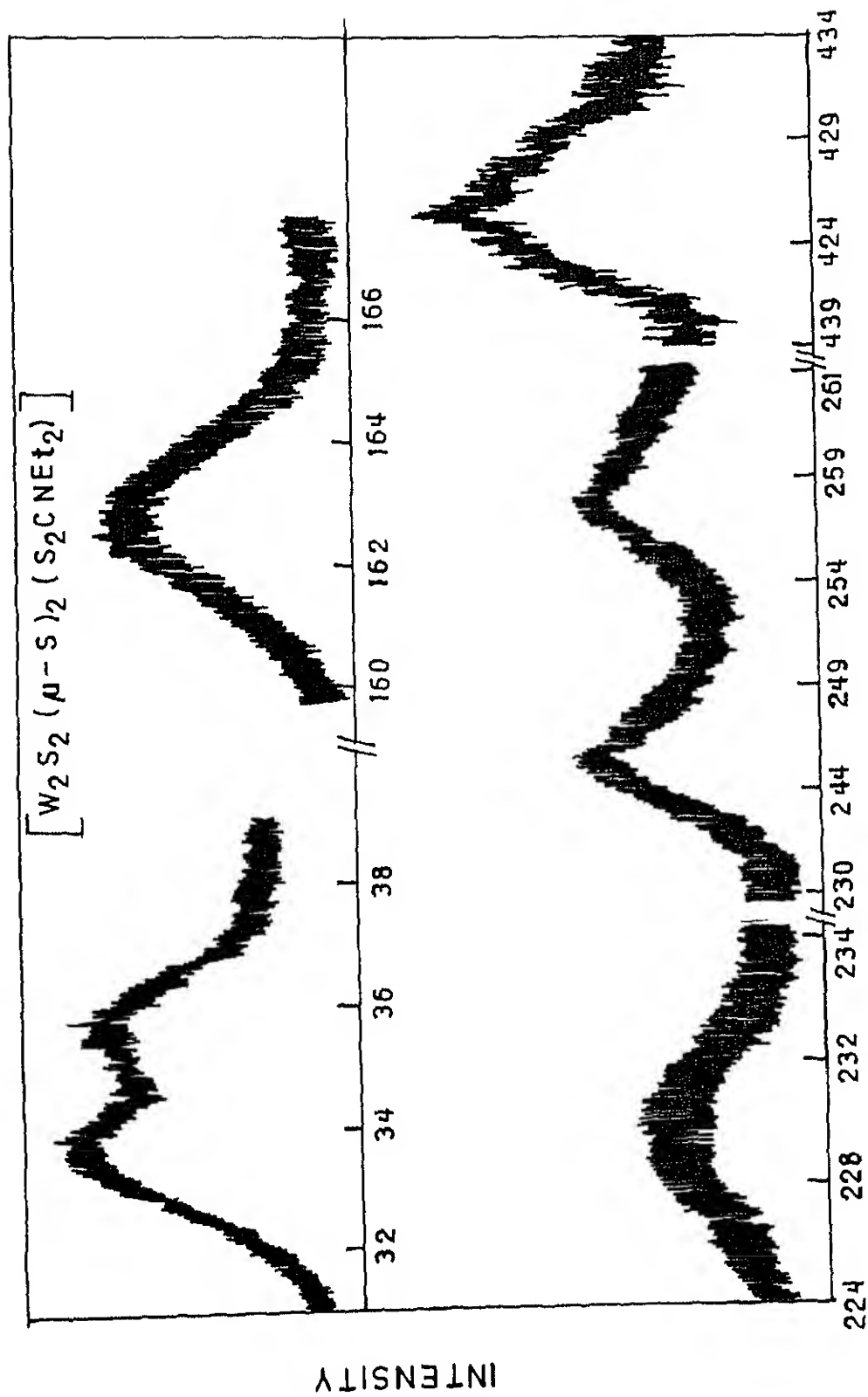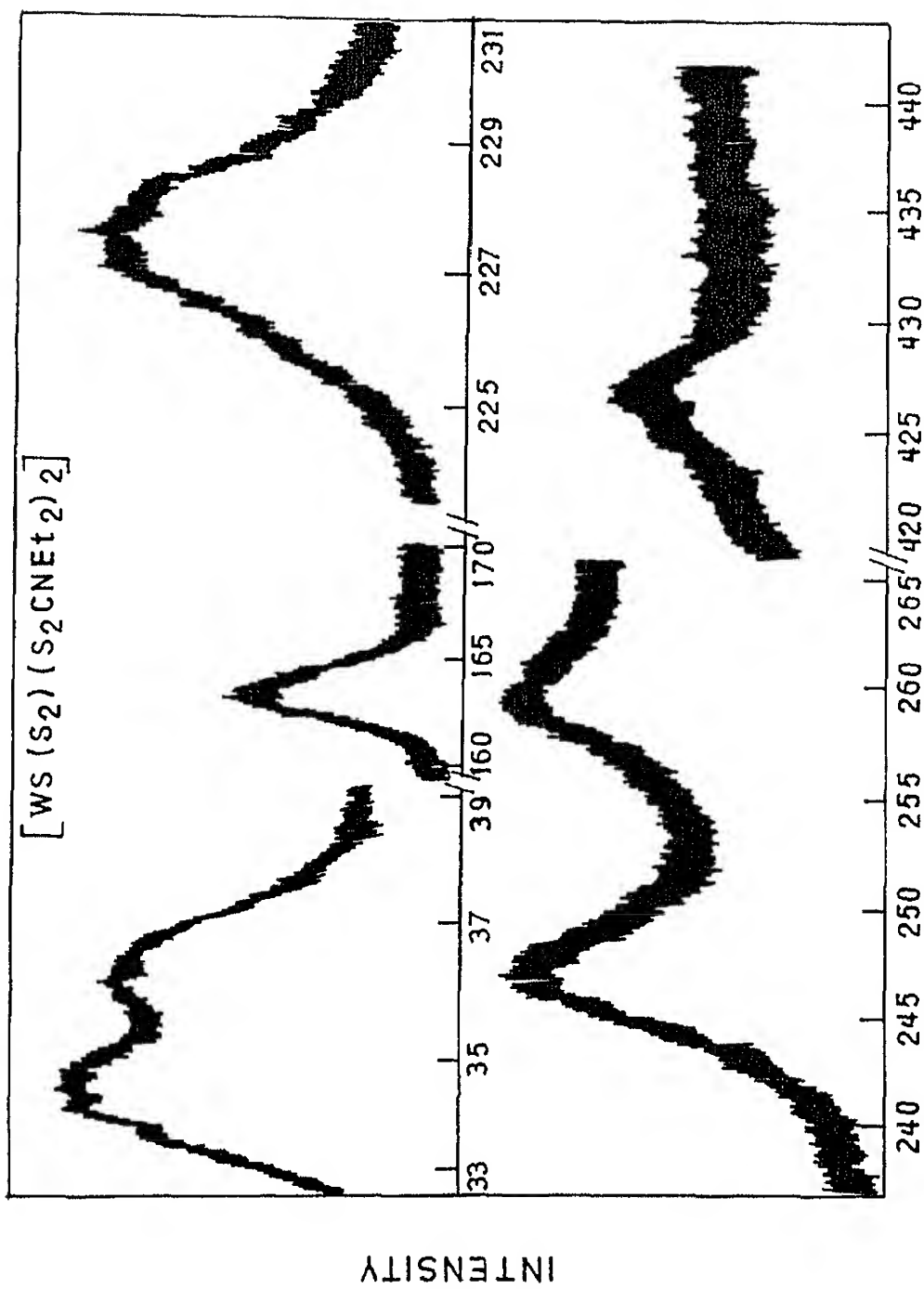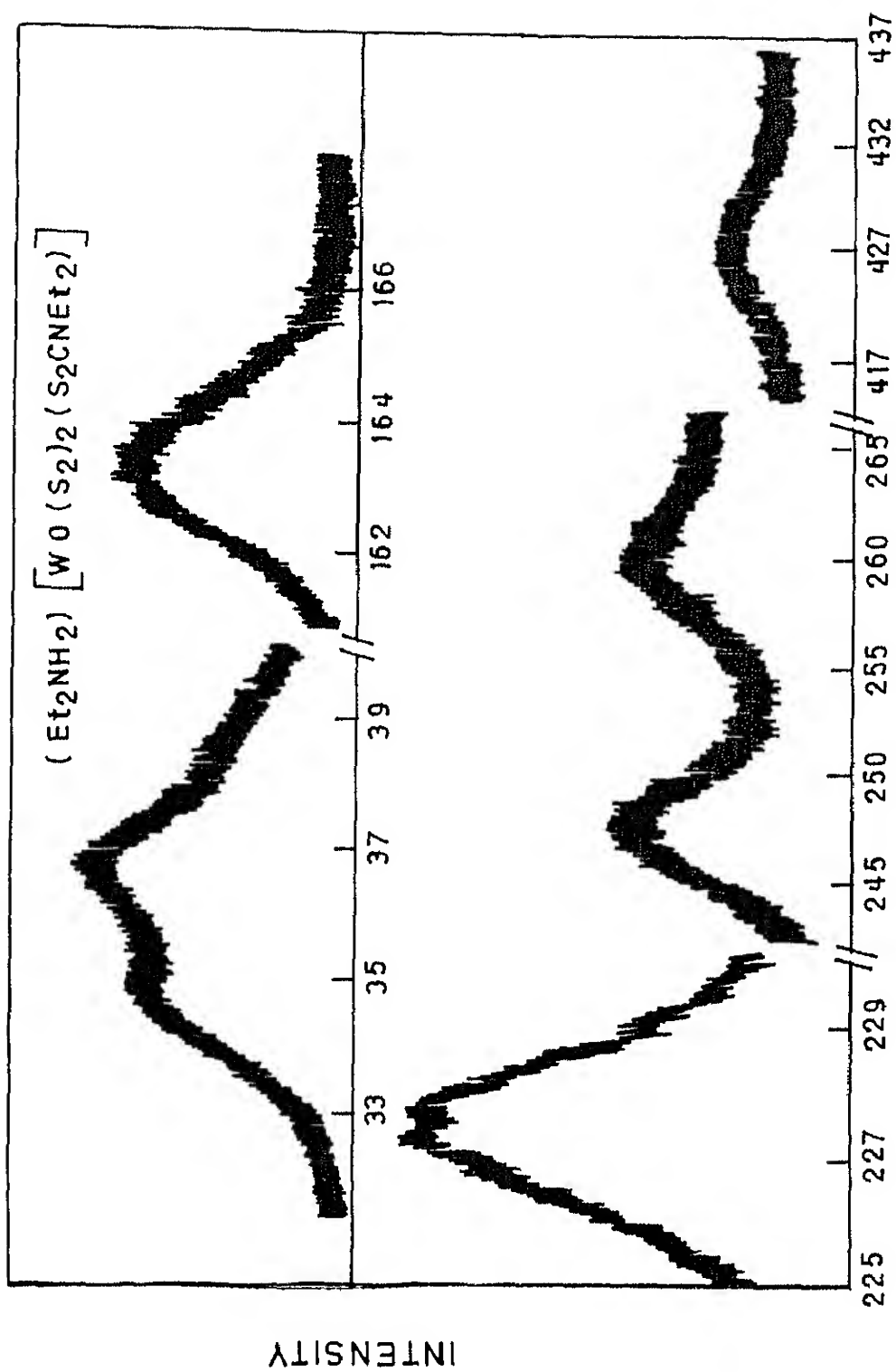
FIG. 4.5.6

complexes containing sulfur, compared to that of elemental sulfur, clearly demonstrate that the sulfur present either in the form of sulfido, persulfido, thiocarbamato or dithiolene, contain formal negative charge.

For the complex ion, $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$, the S(2p) and $S(2s_{1/2})$ values are more negative compared to the corresponding molybdenum analog, $[Mo_2O_2(\mu-S)_2(S_2)_2]^{2-}$. When persulfido ligand is replaced by dithiocarbamato or dithiolene as in complexes $[W_2O_2(\mu-S)(S_2CNEt_2)_2]$ and $[W_2O_2(\mu-S)_2(S_2C_2(COPh)_2)_2]^{2-}$, the S(2p) and $S(2s_{1/2})$ values remain almost unchanged. However, the FWHM for S(2p) in these complexes differ. For the dithiolene derivative the lowest FWHM value (2.6 e.V.) suggests that the bridged sulfido ligand and dithiolene ligand mix so profoundly that the individual identity of these two different types of sulfur atoms is lost. This can be further appreciated by viewing the FWHM of S(2p) in $S_2C_2(CN)_2^{2-}$ which is 2.7 e.V. For the other two complexes, $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ and $[W_2O_2(\mu-S)_2(S_2CNEt_2)_2]$, FWHM values suggest that in principle deconvolution of this band is possible and S(2p) binding energies for bridged sulfido, persulfido, and dithiocarbamato ligand can be deduced following the procedure adopted by Siegbahn.[154] For $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ the broad band for S(2p) binding energy when resolved gave two sets of S(2p) binding energies in the ratio 1:2 at 163.3 and 162.0 e.V. Similarly the band for $[W_2O_2(\mu-S)_2(S_2CNEt_2)_2]$ on resolution gave S(2p) binding energies at 163.1 and 163.5 e.V. On the basis of these values, the S(2p) binding energies for bridged sulfido ligand is assumed

to occur in the range 163.1 - 163.3 e.V. in these complexes.
When there are three different types of sulfur atoms attached
to tungsten, for example, in $[W_2S_2(\mu-S)_2(S_2CNEt_2)_2]$ the S(2p)
binding energy band is very broad (FWHM 3.06). This extra
broadness compared to the corresponding oxo complex, $[W_2O_2(\mu-S)_2-$
$(S_2CNEt_2)_2]$, is accounted for the presence of an additional
sulfur atom at a terminal position. In case of mononuclear
complexes, $[WS(S_2)(S_2CNEt_2)_2]$ & $[WO(S_2)_2(S_2CNEt)]^-$ the S(2p) bind-
ing energy band is very narrow. The low FWHM values in these
cases suggest that the mixing of different types of sulfur atoms
is so effective that any distinction among them is not possible.

The $W(4f_{7/2})$ and $W(4f_{5/2})$ binding energies of these complex-
es show the expected trend. The values are higher for the comp-
lexes where the formal oxidation state is VI. Comparison of
these W(VI) complexes with WO_4^{2-} [155] suggest more electron den-
sity on tungsten in hepta-coordinated species, $[WO(S_2)_2(S_2CNEt_2)]^-$
and $[WS(S_2)(S_2CNEt_2)_2]$. Taking metallic tungsten in zero oxida-
tion state, no meaningful correlation can be made. Any discre-
pancy in these values may be due to different standardization
procedure. However, in the present study, a general correlation
can definitely be made. The expected trend is also reflected in
$W(4d_{5/2})$, $W(4d_{3/2})$ and $W(4p_{3/2})$ binding energies of the complexes
discussed here (Table 4.12).

Table 4.12. Binding Energy (e.V.)

Complex	W(4f$_{7/2}$)	W(4f$_{5/2}$)	S(2p) (FWHM)	S(2s$_{1/2}$)	W(4d$_{5/2}$)	W(4d$_{3/2}$)	W(4p$_{3/2}$)	Ref.
	-	-	164.2	-	-	-	-	157
Mo$_2^V$O$_2(\mu$-s$)_2($s$_2)_2]^{2-}$	-	-	163.2	227.4	-	-	-	69, 86
W$_2^V$O$_2(\mu$-s$)_2($s$_2)_2]^{2-}$	33.9	36.1	162.6 (2.92)	226.7	246.7	260.6	426.9	This work
W$_2^V$O$_2(\mu$-s$)_2($S$_2$C$_2$(COPh)$_2)_2]^{2-}$	33.4	35.6	162.7 (2.60)	226.8	246.7	259.0	425.7	This work
W$_2^V$O$_2(\mu$-s$)_2($S$_2$CNEt$_2)_2]$	33.9	36.1	163.3 (2.87)	227.0	245.7	259.4	426.0	This work
W$_2^V$S$_2(\mu$-s$)_2($S$_2$CNEt$_2)_2]$	33.6	35.7	162.8 (3.06)	227.0	245.2	258.0	426.3	This work
Mo^{VI}O(S$_2$)(S$_2$CNEt$_2)_2]$	-	-	163.2	227.1	-	-	-	69, 86
W^{VI}O(s$_2)_2($S$_2$CNEt$_2)]^-$	34.3	36.3	162.8 (2.60)	226.9	246.8	258.9	426.3	This work
W^{VI}S(S$_2$CNEt$_2)_2]$	34.6	37.3	163.2 (2.60)	227.6	246.9	259.4	425.4	This work
a$_2$[W^{VI}O$_4$]	37.9	39.7	-	-	249.0	262.3	-	155
s$_2$[W^{VI}s$_4$]	35.9	37.7	162.8	-	247.6	259.8	-	155
(foil)	34.0	37.0	-	-	246.0	259.0	426.0	157

X-Ray Powder Diffractograms

X-ray powder diffractograms of $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ and $[W_2O_2(\mu-S)_2(S_2CNEt_2)_2]$ (Figs. 4.5.7 and 4.5.8) were recorded to make a comparison with the corresponding molybdenum complexes. The powder pattern of these compounds was found to be similar to those of their molybdenum analogs. This suggests that $[W_2O_2(\mu-S)_2(S_2)_2]^{2-}$ and $[W_2O_2(\mu-S)_2(S_2CNEt_2)_2]$ could be isostructural to their molybdenum analogs.[32,158] A comparison of X-ray powder pattern of $[WO(S_2)(S_2CNEt_2)_2]$ with $[WS(S_2)(S_2CNEt_2)_2]$ (Fig. 4.5.9) suggests that these two are also isostructural.

X-Ray Crystal Structure of $(Et_2NH_2)[WO(S_2)_2(S_2CNEt_2)]$

Crystal data of $(Et_2NH_2)[WO(S_2)_2(S_2CNEt_2)]$ are presented in Tables 4.13 - 4.17. The structure with bond distances (Fig. 4.5.10) shows that W(VI) is seven coordinate with a terminal oxygen, two edge-bound S_2^{2-} and one chelated $(S_2CNEt_2)^-$ ligand arranged in a pentagonal bipyramidal polyhedron. The S_2^{2-} ligands and one sulfur of the dithiocarbamate ligand lie in the equatorial plane. Oxygen and the second sulfur of the dithiocarbamate ligand occupy the axial positions. It is interesting to note that the tungsten atom lies 0.32 Å above the mean plane through S1-S5 (Fig. 4.5.10). Another feature worth noting is that $W-S_6$ (sulfur of the dithiocarbamate unit) trans to oxygen is (2.605 Å) significantly longer than the equatorial $W-S_5$ bond (2.510 Å).

$(Et_4N)_2 \left[Mo_2 O_2 (\mu{-}S)_2 (S_2)_2 \right]$

$(Et_4N)_2 \left[W_2 O_2 (\mu{-}S)_2 (S_2)_2 \right]$

INTENSITY

$2\theta \, [°]$
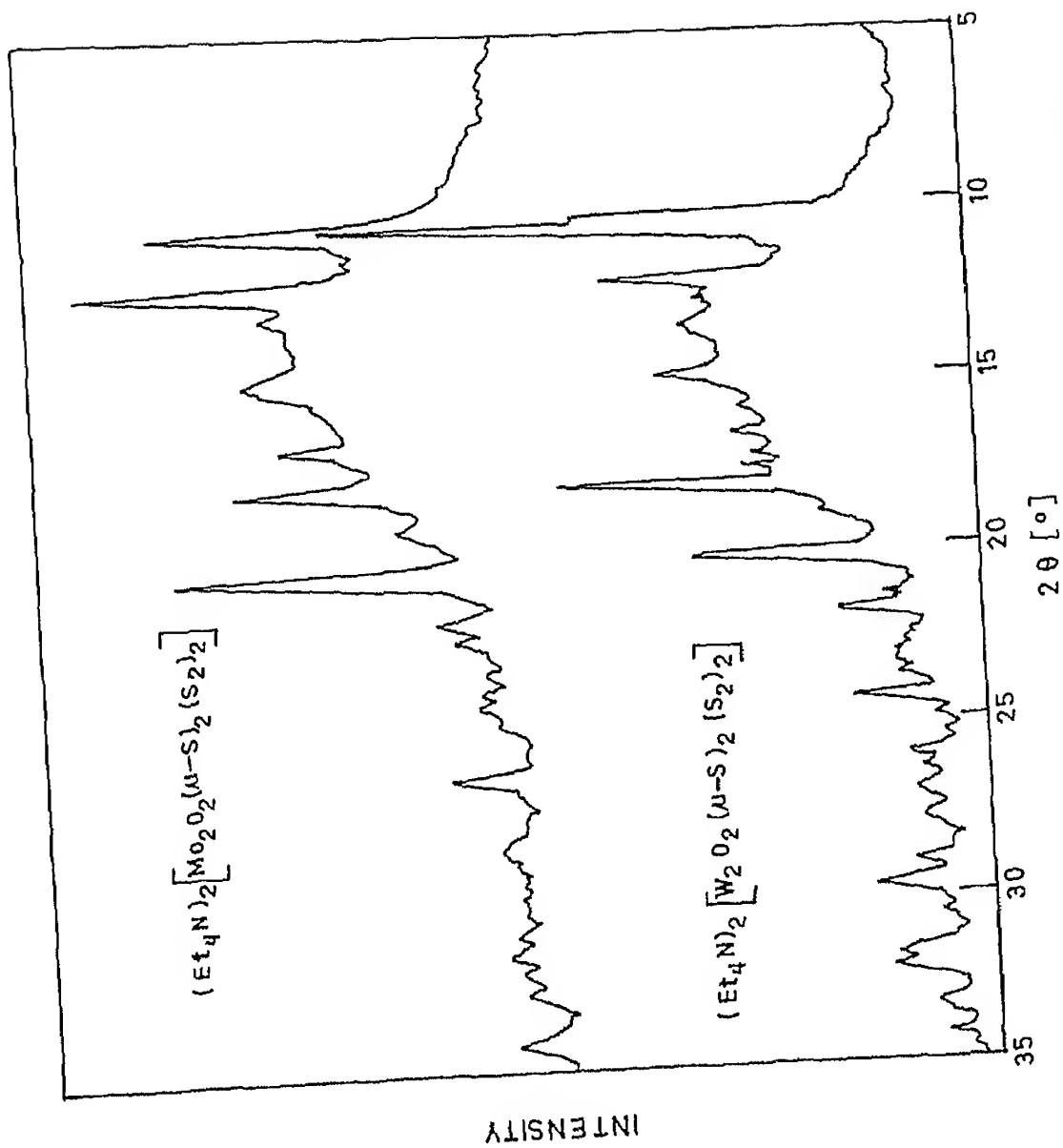
FIG 4.5.7 X-RAY POWDER DIFFRACTOGRAMS
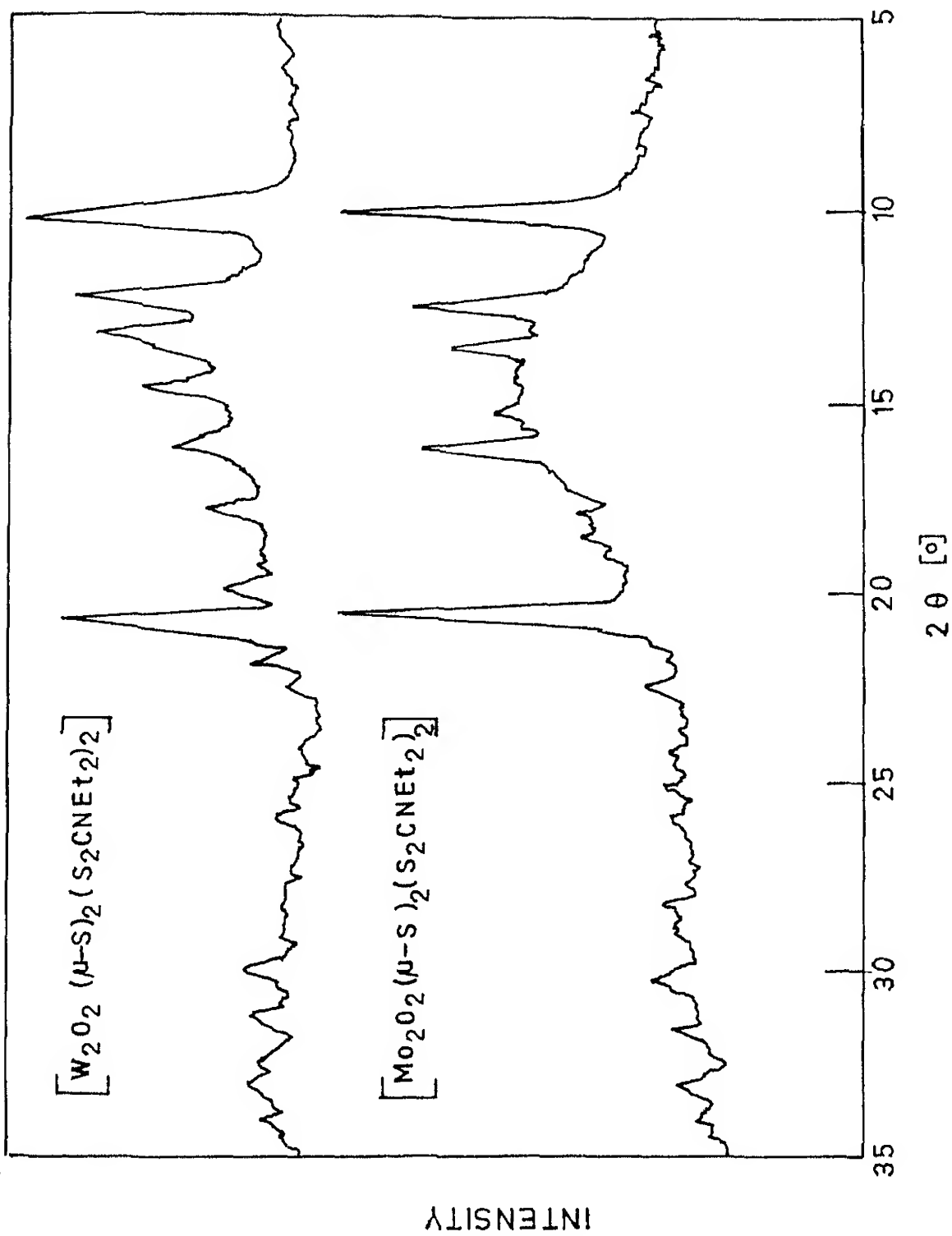
FIG 4.5.8 X-RAY POWDER DIFFRACTOGRAMS

$\left[W_2O_2(\mu-S)_2(S_2CNEt_2)_2\right]$

$\left[Mo_2O_2(\mu-S)_2(S_2CNEt_2)_2\right]$

INTENSITY

2θ [°]
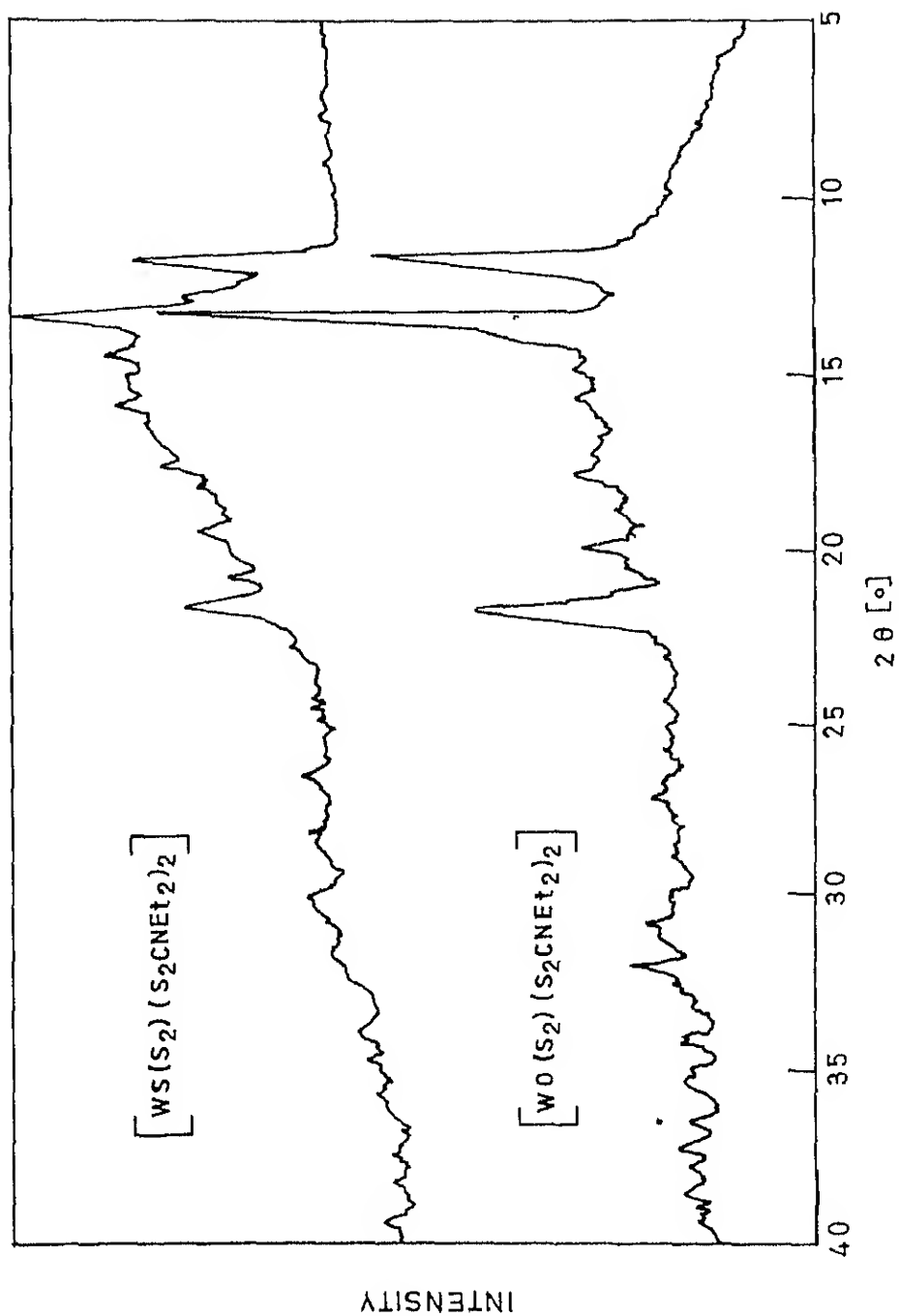
FIG 4.5.9 X-RAY POWDER DIFFRACTOGRAMS

Table 4.13   Summary of Crystal Data

Lattice Dimensions*	$a = 14.500(6)$ Å
	$b = 13.434(5)$ Å
	$c = 10.174(4)$ Å
	$\beta = 105.06(3)$ Å

Volume of unit cell (V) $1913.9 Å^3$

Number of Molecular   4
Units in unit cell (Z)

Density $1.91 \ g/cm^3$

Space group $P2_1/C$ (monoclinic)

Radiation MoK_α $(67.90 \ cm^{-1})$

Least squares refinements converged at an R value of

0.060 for 3555 independent reflections $[F_o > 3.92 \ (F_o);$

$4° < 2\theta < 54°]$

---

*Values in brackets are the standard deviations

(ET2NH2) [WO(S2)2(ET2DTC)]
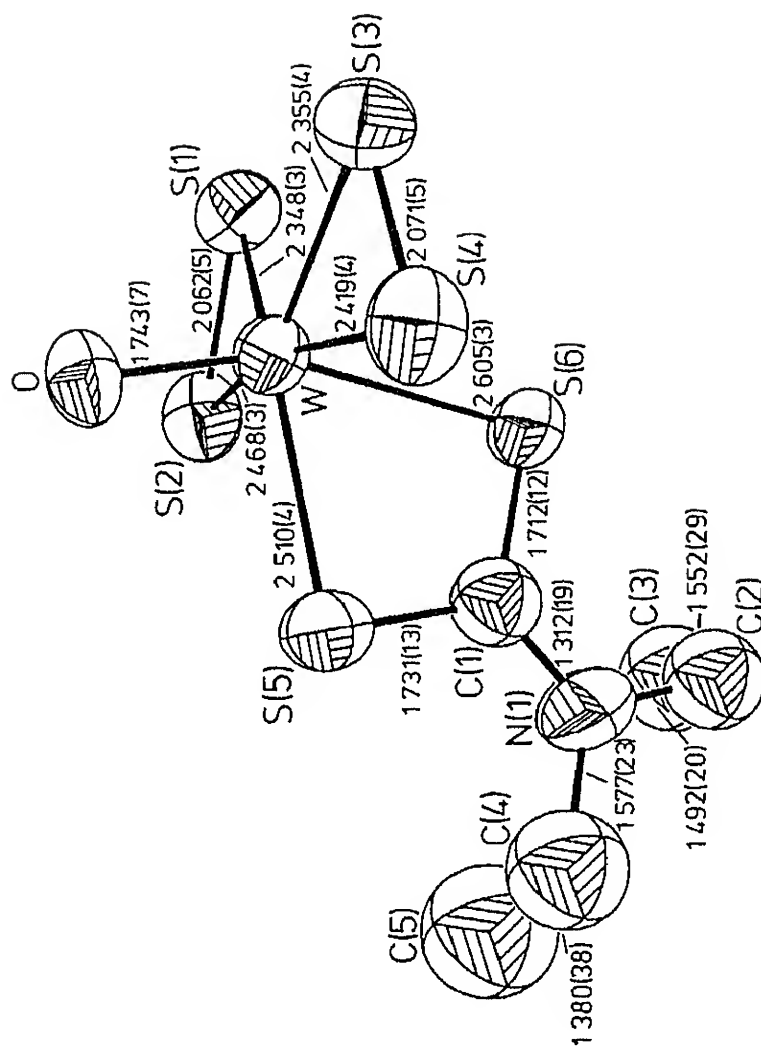
FIG 4.5 10

Table 4.14 Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\mathring{A}^2 \times 10^3$)

	x	y	z	U
W	2155(1)	457(1)	2347(1)	51(1)*
S(1)	2378(2)	2181(2)	2207(3)	67(1)*
S(2)	2645(2)	1426(2)	581(3)	68(1)*
S(3)	1949(3)	828(3)	4515(3)	76(1)*
S(4)	2093(3)	-676(3)	4168(4)	78(1)*
S(5)	2733(2)	-1049(2)	1337(4)	77(1)*
S(6)	4000(2)	255(2)	3241(3)	65(1)*
O	1008(5)	252(5)	1314(7)	60(2)*
N(1)	4614(9)	-1358(9)	2179(12)	91(5)*
N(2)	486(7)	3984(6)	3509(8)	61(3)*
C(1)	3891(10)	-796(9)	2261(12)	70(3)
C(2)	5609(13)	-1072(12)	2910(16)	96(4)
C(3)	6071(17)	-347(14)	2079(21)	121(6)
C(4)	4438(17)	-2411(14)	1471(21)	123(6)
C(5)	4542(24)	-2228(20)	182(28)	170(10)
C(6)	12(9)	2977(8)	3330(11)	68(3)
C(7)	-216(11)	2680(10)	4619(13)	81(3)
C(8)	742(9)	4388(8)	2294(11)	66(3)
C(9)	1191(13)	5429(11)	2613(16)	93(4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 4.15 Bond lengths ($\mathring{A}$)

W-S(1)	2 348(3)	W-S(2)	2.468(3)
W-S(3)	2.355(4)	W-S(4)	2 419(4)
W-S(5)	2.510(4)	W-S(6)	2.605(3)
W-O	1.743(7)	S(1)-S(2)	2.062(5)
S(3)-S(4)	2.071(5)	S(5)-C(1)	1.731(13)
S(6)-C(1)	1.712(12)	N(1)-C(1)	1.312(19)
N(1)-C(2)	1.492(20)	N(1)-C(4)	1.577(23)
N(2)-C(6)	1.507(15)	N(2)-C(8)	1.482(16)
C(2)-C(3)	1.552(29)	C(4)-C(5)	1.380(38)
C(6)-C(7)	1.489(20)	C(8)-C(9)	1.542(18)

Table 4.16   Bond Angles (θ^O)

S(1)-W-S(2)	50.6(1)	S(1)-W-S(3)	84.3(1)
S(2)-W-S(3)	134 5(1)	S(1)-W-S(4)	134 5(1)
S(2)-W-S(4)	164.9(1)	S(3)-W-S(4)	51 4(1)
S(1)-W-S(5)	134.8(1)	S(2)-W-S(5)	86.4(1)
S(3)-W-S(5)	133.7(1)	S(4)-W-S(5)	83.6(1)
S(1)-W-S(6)	88.8(1)	S(2)-W-S(6)	81.2(1)
S(3)-W-S(6)	93 6(1)	S(4)-W-S(6)	84.6(1)
S(5)-W-S(6)	68.7(1)	S(1)-W-O	104.1(2)
S(2)-W-O	93.1(3)	S(3)-W-O	105.3(3)
S(4)-W-O	98.2(3)	S(5)-W-O	89.7(3)
S(6)-W-O	157.8(3)	W-S(1)-S(2)	67.7(1)
W-S(2)-S(1)	61.7(1)	W-S(3)-S(4)	65.9(1)
W-S(4)-S(3)	62.7(1)	W-S(5)-C(1)	90.0(4)
W-S(6)-C(1)	87.3(5)		

Table4.17 Anisotropic thermal parameters ($\mathring{A}^2 \times 10^3$)

	U11	U22	U33	U23	U13	U12
W	42(1)	56(1)	56(1)	-0(1)	13(1)	0(1)
S(1)	61(2)	58(1)	82(2)	-2(1)	21(1)	-3(1)
S(2)	55(1)	86(2)	66(1)	8(1)	22(1)	-6(1)
S(3)	77(2)	89(2)	67(2)	-2(1)	28(1)	8(2)
S(4)	75(2)	82(2)	78(2)	20(1)	19(2)	-2(2)
S(5)	64(2)	74(2)	90(2)	-24(1)	14(2)	6(1)
S(6)	44(1)	73(2)	73(2)	-12(1)	7(1)	8(1)
O	47(4)	76(4)	54(4)	2(3)	5(3)	-7(3)
N(1)	72(7)	97(8)	103(8)	-23(6)	20(6)	27(6)
N(2)	66(6)	63(5)	58(5)	-1(4)	20(4)	11(4)

The anisotropic temperature factor exponent takes the form.
$-2\pi^2$ $h^2 a^{*2}$ U_{11} + ...+ 2hka*b*U_{12}

The asymmetric tungsten-sulfur distances originating from bound $S_2{}^{2-}$ is large, consistent with the structural unit in which the sulfur atoms, from two persulfido ligands are approximately trans to each other.[144,145] Similar asymmetry are found for some O_2 complexes in which the ligand is coordinated side on to the metal.[159]

CONCLUSION

Application of Induced Electron Transfer Reactions to tungsten-sulfur systems is a recent phenomenon. Invoking this comparatively newer methodology as synthetic strategy, various mono-, bi- and trinuclear complexes having tungsten in different oxidation states, ranging from +4 to +6 have been synthesized. In some cases, the intermediate species could be identified and probable mechanisms have been proposed. Wherever molybdenum analogs were known, a comparative study has been made. On this basis and other conventional physico-chemical studies, structures of the complexes have been proposed. Only in the case of $(R_2NH_2)[WO(S_2)_2(S_2CNR_2)]$ which does not have its molybdenum analog, assignment of structure, merely on the basis of conventional physicochemical studies was a problem. Thus, the molecular structure of $(Et_2NH_2)[WO(S_2)_2(S_2CNEt_2)]$ was determined and the formation of first bispersulfido-tungsten complex has been established.

This work will certainly be of some help to understand the mechanistic and functional aspects of the recently discovered tungsto-enzyme, formate dehydrogenase. Moreover, this is an entirely new approach in synthetic inorganic chemistry. The

field is still in the embryonic stage and many more questions
are yet to be answered. Hence, at this stage one then perhaps
recalls what Taube said, "At this stage, it would be premature
to attribute the difference to effects of the kind we are
searching for, but it would be equally premature to give up
the search at this stage."

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